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ORIGINAL CONTRIBUTION

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Evaluation of polymeric flocculants for oily water systems using a photometric dispersion analyzer

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Abstract During oil production and treatment, oil-in-water (O/W) emulsions are formed. These dispersions require treatment prior to disposal. In order to improve oil/water separation processes through any physical process (decanting, flotation, centrifuging etc), the particle size of the dispersed phase should be increased. This may be obtained by a flocculation process, which consists in the agglomeration of several particles or drops using as flocculating agent hydrophilic high molecular weight macromolecules. Poly (ethylene-b-propylene oxide) and poly (vinyl alcohol) polymers have been evaluated as flocculating agents for oily water systems. Their performance is related to the particle size increase of the dispersed phase. In this work, a photometric dispersion analyzer (PDA) has been used to accomplish the oil drop agglomeration. Synthetic as well as produced water was used. Data are in good agreement with previous tests. Qualitative information related to aggregates or particle size distribution of the oily water systems can be obtained using PDA.

Keywords Flocculants · Emulsions · Poly(ethylene-b-propylene oxide) · Poly(vinyl alcohol)

Introduction

Petroleum-derived seawater pollution is a consequence of the increasing energy requirement experienced by present western patterns, as well as the high ratio of petroleum-related products in the present energy system. Environmental impact resulting from disposal of produced water is normally evaluated on the basis of the compound's toxicity as well as by the amount of organic compounds present therein. In order to secure the quality standards in the disposal of produced water, the National Council for the Environment (CONAMA-Brazil) has set that the maximum acceptable levels for oil and grease disposal of produced water should be ≤ 20 mg/L [1, 2].

The reduced size of the dispersed oil drops present in oily water produced during oil production processes is the main drawback to be by-passed during the treatment of such waste. The most viable alternative to attain the effective removal of such oil is to increase the size of the dispersed drops followed by separation by physical methods (decantation, centrifugation, membrane filtration, flotation, etc.). The aggregation process of oil droplets is made possible through the use of compounds having affinity for both phases (through interaction among the dispersed oil drops) and working as a link between them. Such a process is known as flocculation and the substances that promote this phenomenon are known as flocculating agents [3, 4].

The oily water generated in the petroleum industry is often formed by an emulsion corresponding to a colloidal dispersion of a non-polar fluid dispersed in water. Emulsions are colloidal systems formed by a liquid partitioned in small droplets (called dispersed phase or internal phase) dispersed in another immisci-

ble liquid, called dispersing phase or continuous phase. As are all colloidal dispersions, emulsions are intrinsically unstable and the dispersed phase drops tend to coalesce, forming a liquid macroscopic phase. In the case of produced water, there is produced an oil-in-water (O/W) emulsion stabilized by natural surfactants present in the system and/or deriving from additives used during the petroleum producing processes [3, 5, 6]. According to the literature, the four distinct processes identified in an emulsified system are: breaking [6], creaming [6, 7], flocculation [6, 8], and coalescence [6, 8]. Specifically in the case of the treatment of petroleum industry-derived oily waters, the process involves destabilization of the issued emulsion, that is, the system flocculation [4, 8].

The continuous monitoring of the particle or drop aggregation process is made possible with the aid of an instrument named photo dispersion analyzer–PDA 2000. This instrument allows detection of particle formation or dispersion flocculation in the early stages of such processes; this not being possible with most other current techniques. This technique has been successfully used to study the aggregation kinetics of high molecular weight poly(ethylene oxide) at temperatures above the solution cloud points [9]. The PDA operation principle is based on the fact that dispersions may show a slight fluctuation in their local composition. The technique provides three distinct response modes:

1. The *dc* component, associated to the suspension turbidity, that is, the higher the system turbidity the lower will be the value of this component
2. The *rms* component, corresponding to the average square root of the particle concentration in the suspension, this component being associated to the particle size—higher *rms* values corresponding to particle appearing or to increased particle aggregates (flocculation process)
3. The *ratio* component, related to the response values for the *rms* and *dc* components (ratio = 10×rms/dc) [10, 11, 12, 13, 14]

Experimental

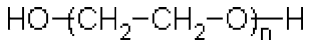
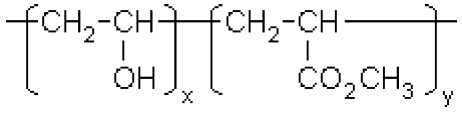
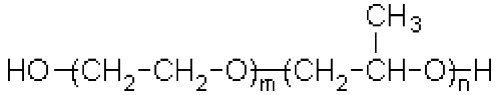
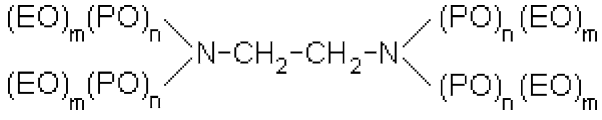
Materials

Commercial polymers used as flocculants are described in Table 1 [15]. Two commercial flocculants were also used, here designated by Floc A and Floc B (Clariant) and a latex sample (Petroflex, Brazil).

Preparation of synthetic emulsions

In order to reproduce the marine environment, brine having a salt concentration of 55,000 ppm (250 g/L of

Table 1 Characterization data of the commercial polymers [15]

Polymer	Chemical structure	Molecular weight	Hydrolysis degree (%)	EO/PO ratio (%w/w)
PEO 11		4.8×10^{6} [a]	–	–
PEO 12		5.2×10^{6} [a]	–	–
PEO 13		6.5×10^{6} [a]	–	–
PVA 13		260,000 [a]	87.9 [c]	–
PVA 14		67,000 [a]	87.8 [c]	–
PEO-PPO 11		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

sodium chloride and 25 g/L of calcium chloride) was prepared. Using a Turrax PT 3100 blender at a rotating speed of 13,000 rpm, an oil aliquot (approximately 0.8 mL for each liter of brine) was slowly added (addition period ~9 min), using a long stem syringe. Upon completion 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 another portion of brine (one and a half times the amount used in the beginning of the preparation). This system was then submitted to a 5,000-rpm agitation for 5 min.

Particle aggregation study

Particle aggregation study of the dispersions was carried out with the aid of a model PDA 2000 photo dispersion analyzer, manufactured by Rank Brothers. The addition of the flocculating agent was gradual and uniform, keeping time intervals between the polymer additions and subsequent reading of the obtained values for each of the three response answers. For more concentrated systems, pipes having internal diameter of 1 mm and flow rate of 2.5 mL/min were used. Less concentrated systems were analyzed in a 3-mm pipe, at a flow rate of 20 mL/min. Agitation of the dispersion was kept in the range 100–200 rpm.

Results and discussion

It is important to stress that according to the information supplied with the instrument [13], quantitative interpretations in terms of particle or aggregate size distribution are not feasible. However, data supplied by the instrument provide a very convenient empirical indication related to the aggregation state shown by the tested system. This allows the assessment of an optimum dosage of the flocculating agent, for maximum reached response values of the rms and rms/dc ratio, this being an indication of the boosting of the aggregation effect.

When the disaggregation phenomenon occurs (breaking of the freshly formed aggregates), caused by the addition of a dispersing agent or by the shearing effect (caused by the agitation imposed to the system), the response values of the rms and rms/dc components undergo a significant reduction and attain a minimum value, when the particles are completely dispersed. The dc component follows the turbidity variation of the system as a whole; the dc gradual reduction is observed as a consequence of the increase in particle number and with the increased aggregation in the system, the dc variation being much more affected by particle number associated effects.

Synthetic oily water/flocculating agent system

This study aimed at obtaining a better understanding of the flocculation process kinetics of the water-dispersed oil droplets derived from offshore oil production systems (salinity and size distribution of the emulsified similar oil droplets) that should be treated before being discarded.

PDA 2000 was chosen to perform this study since it is able to detect particle formation (or dispersion flocculation) in the initial steps of those processes and therefore it is capable of a step-by-step monitoring of the gradual increase in dispersed oil droplet size, such an increase being due to the action of flocculating agents. Thus, flocculation tests were designed to evaluate the effect of the gradual variation in concentration of flocculant added to the synthetic oily water/flocculating agent system.

The same polymers employed as flocculating agents in a previous study [15] on the flocculation process in synthetic oily water/flocculating agent systems were evaluated in the flocculation/flotation study. However, the study using PDA 2000 aimed at a better understanding of how the flocculation process occurs (size increase of the dispersed oil drops) and how the flocculant concentration can influence the aggregation process (assessment of the flocculating agent optimum concentration). Thus, the efficiency of a polymer as flocculant can be evaluated as a function of its ability to yield bigger aggregates, those being easier to remove by physical separation processes such as flotation.

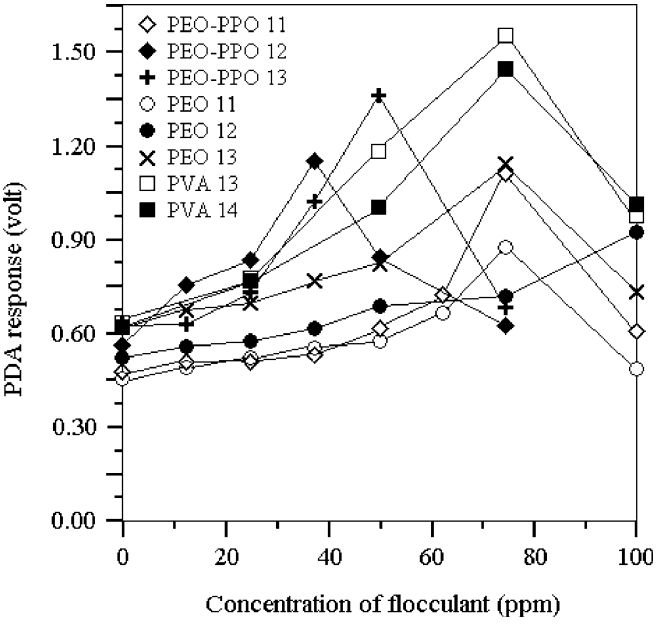


Fig. 1 PDA response variation (rms) as a function of the flocculating agent concentration added to the oil/water emulsified system

Figure 1 plots the PDA 2000 response curves (rms component) obtained from the variation in the concentration of flocculating agent added to the oil-in-water emulsified system. It may be observed that at lower concentrations, PEO-PPO 12 performs better, since its optimum addition concentration (curve maximum) is at a concentration range lower than those of other polyoxide-based copolymers and also lower than that of the remaining polymers. From a comparison between PEO-PPO 11 (linear structure and EO/PO ratio = 3.5), PEO-PPO 12 (linear structure and EO/PO = 6.2), and PEO-PPO 13 (non-linear structure and EO/PO = 8.6) the relevance of the hydrophilic–lipophilic balance is made obvious. Also evident is the relevance of the way the oxyethylenic groups are distributed in the polymer chain on the performance of an additive as flocculant. Polyvinyl alcohol-based polymers PVA 13 and PVA 14 have shown the highest response values at relatively higher concentrations. In flocculation tests, the PEO-based polymers had the worse response results in PDA. This is because a higher flocculant concentration was required, in spite of the fact that in PEO 13 tests the response values were close to the values for polyoxide-based copolymers. It is possible to improve this performance by chemical modification reactions involving the introduction of small hydrophobic groups into one of the polymer chain ends, thus making it possible that high molecular weight poly (ethylene oxide) molecules have in one of their chain ends a group having a high affinity for the oily phase.

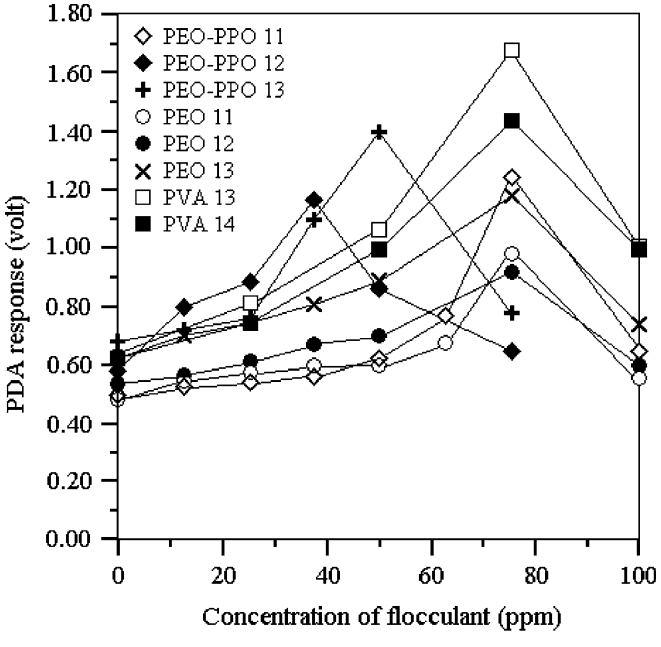


Fig. 2 PDA response variation (rms/dc ratio) as a function of the flocculating agent concentration added to the oil/water emulsified system

Figure 2 plots the PDA response curves (rms/dc ratio) obtained by varying the concentration of flocculating agent added to the oil-in-water emulsified system. The values attain a maximum that can be associated with the optimum flocculation concentration. Those curves took a behavior similar to that drawn for Fig. 1, thus confirming the considerations assumed in the rms component response, relative to the individual flocculation process of the tested polymers.

Results obtained from PDA 2000 are consistent with the previously obtained [15] particle size distribution using the Mastersizer (Malvern) instrument. PVA 13 and PVA 14 polymers, having higher response values, also had the higher values for average particle size. This confirms that the response intensity in PDA 2000 is associated with the dimensions of particles generated in the system.

Produced oily water/flocculating agent system

Selected polymer materials were evaluated for their flocculating action in produced oily water. Results indicate low performance and no relationship to structure, composition, or molecular weight, obtained in the study in synthetic oily water. In order to compare with the results obtained for the selected polymers, the oily water was then treated with commercial polymeric flocculants Floc A and Floc B, these being made up of a cationic polyelectrolyte. Tests were carried out according to two distinct modes: (i) by observing the PDA 2000 response as a function of the flocculant concentration at a constant measurement time, and (ii) by keeping the flocculant concentration constant and observing the instrument response as a function of time.

Flocculation tests as a function of flocculant concentration

Flocculation tests conducted at varied concentrations of flocculating agent were run aiming at determining the optimum performance concentration range. Results obtained for Floc A and Floc B are shown in Figures 3a and b, respectively, In Fig. 3a it my be observed that, according to the response provided by the rms component (chosen since it best characterizes the flocculation process), Floc A was able to work in a more effective way in the size increase of the particle aggregates at a concentration in the range of 150 to 200 ppm. Figure 3b shows the curves obtained for Floc B. Still analyzing the rms response, it may be observed that the optimum working range for this flocculant is 100–240 ppm. From a comparison between the two systems, two facts may be observed: Floc B shows optimum flocculation concentration at a lower concentration than that of Floc A. However, its aggregation efficiency is lower than that of

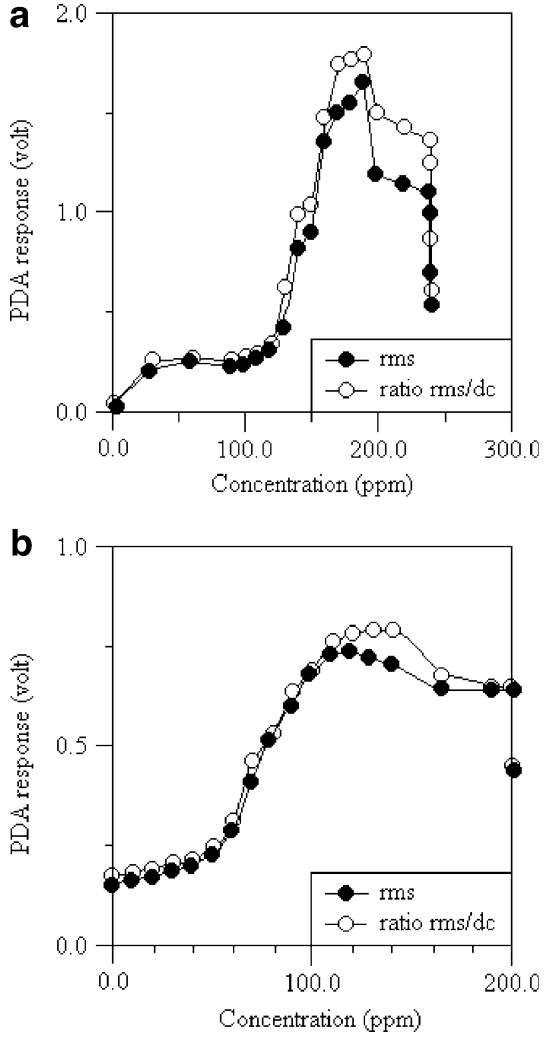


Fig. 3a, b Influence of the flocculating agent concentration variation on the flocculation of a produced oily water system. **a** Floc A. **b** Floc B

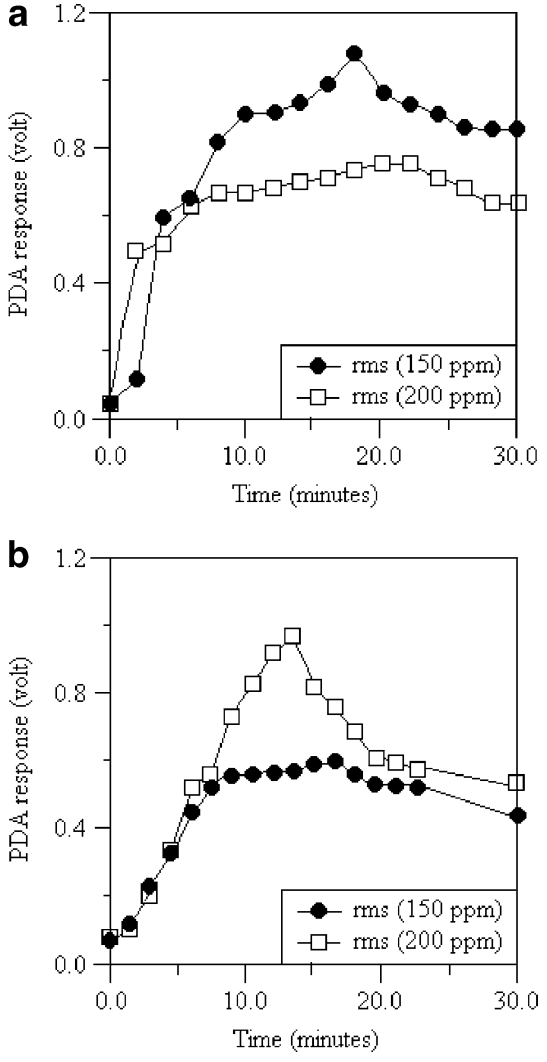


Fig. 4a, b Comparative study of the effect of time on the flocculation phenomenon in a produced oily water system, as a function of the concentration variation of the flocculating agent at concentrations of 150 and 200 ppm, added in one single shot. **a** Floc A **b** Floc B

Floc A, as can be observed from the intensity of the rms response.

Flocculation test as a function of time, at constant flocculant concentration

Flocculation tests as a function of time were run for commercial flocculants Floc A and Floc B for the concentrations of 150 and 200 ppm. Those concentrations were set forth according to the previously obtained results. Figures 4a and b show the results obtained for Floc A and Floc B (at concentrations of 150 and 200 ppm), respectively. For all cases it can be observed that the system aggregation state varies as a function of time, independently of the flocculant concentration.

Aggregation kinetics can be observed by the rms response. Figure 4a shows that a more favorable aggregation state is reached at a concentration of 150 ppm. In principle this result would not be expected since higher rms values are reached at a higher concentration when the tests are run at short times. However, by observing the behavior of the Floc A-containing system, at short times the results are consistent, that is, the rms value at 200 ppm is higher than that at 150 ppm. Figure 4b shows that a state of higher aggregation is reached at 200 ppm.

The same differences as for the behavior as a function of time occurring in the Floc A-containing system are also observed in this case. The 200 ppm curve shows a maximum rms value with time, characterizing the

re-dispersion effect occurring at long analysis times. This result is highly consistent since re-dispersion is favored by an excess flocculant and, according to Fig. 3b, 200 ppm is already well above the flocculating agent optimum concentration range.

For produced oily water, commercial polymeric flocculating agents have shown superior performance as compared to the selected polymers. However, the study using synthetic oily water and polymeric materials of known structure, composition and molecular weight has made possible a systematic evaluation of these parameters in the flocculation process.

Conclusions

The versatility of the photometric dispersion analyzer (PDA 2000) allows its use in the study of the process involved in dispersion formation or precipitation. The maximum response values for the rms and rms/dc components are related to the larger average diameter of particles or drops. Thus it is possible to identify the optimum dosage of the flocculating agent, in spite of the fact that quantitative interpretations in terms of size distribution of particles or aggregates are not possible with this instrument. Due to its versatility, ease of operation, and reduced dimensions, PDA 2000 may be recommended for utilization in oil production field tests.

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References

1. Huang JS, Varadaraj R (1996) J Colloid Interface Sci 1:535
2. CONAMA (1986), Resolução do Conselho Nacional do Meio Ambiente, CONAMA # 20
3. Lissant KL (1988) Colloid Surf 29:1
4. Hunter RJ (1991) Foundations of colloid science, vol 1. Oxford University Press, New York
5. Woods DR, Diamadopoulos E (1988) Surfactant Sci Ser 28:369
6. Kitchener JA, Mussellwhite PR (1972) The theory of stability of emulsions. Imperial College of Science and Technology, London
7. Manoj P, Fillery-Travis AJ, Watson AD, Hibberd DJ, Robins MM (1998) J Colloid Interface Sci 207:283
8. Saether O, Sjöblom J, Verbich SV, Mishchuk NA, Dukhin SS (1998) Colloid Surf A 142:189
9. Pang P, Englezos P (2002) Colloid Surf A 204:23
10. Quali L, François J, Pefferkorn E (1999) J Colloid Interface Sci 215:36
11. Kawaguchi H, Hoshino H, Amagasa H., Othsuka Y (1984) J Colloid Sci Interface Sci 97:465
12. Ottewill RH, Satgurunathan R (1997) Colloid Polym Sci 265:845
13. Rank Brothers (1999) Photometric dispersion analyzer—PDA 2000. Operating manual, version 1.1. (Revised July 1999)
14. Gregory J (1985) J Colloid Interface Sci 105:357
15. Fernandes RS, González G, Lucas EF (2004) Colloid Polym Sci (accepted for publication)