

Polymer science applied to petroleum production*

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Abstract: The science of polymers, more specifically, synthesis, characterization, and physicochemical properties in solutions, has wide application in the petroleum industry, which uses polymers as components of fluids or additives to correct problems that affect oil production and/or increase production costs. Polymers are utilized during all phases, from drilling to treatment of oil and water. Research on the synthesis of polymers and their respective characterization aims to develop new molecules, with controlled structures, for various applications, having one or more objectives, namely: (1) to enhance operating efficiency; (2) to reduce costs; and (3) to elucidate mechanisms of action that can help in the development of new technologies. The evaluation of the physicochemical properties of a polymer in solution in many cases permits establishing useful correlations between its properties and performance in a specific application, besides providing insight into the mechanisms inherent in the production system, as is the case of stabilization of asphaltenes. Our research group has applied the knowledge of polymer science to the petroleum industry, focusing on the following functions: viscosification, inhibition of clay swelling, formation of filter cake, drag reduction, divergence, modification of wax crystals, stabilization of asphaltenes, emulsification, demulsification, and cleaning of solids systems contaminated with petroleum, among others.

Keywords: oil production; viscosification; inhibition of clay swelling; filter cake; drag reduction; divergence; modification of wax crystals; stabilization of asphaltenes.

INTRODUCTION

The petroleum industry is composed of various upstream and downstream segments, from prospecting for oil to production of petrochemicals. One area of the petrochemical sector involves the production of monomers and polymers, which have applications in a wide variety of sectors, including the petroleum industry itself, which consumes a vast array of oligomer/polymer products. The polymer materials used in the oil industry can be classified into two large groups: (1) solid-state polymers, such as engineering materials, and (2) polymers in solution, employed as components of fluids or additive formulations. Engineering materials include those classified as plastics, fibers, and elastomers in general, for use on offshore platforms, construction of pipelines and floating structures, among others. In solution, polymers are added to fluids or formulations to modify their properties and are used in many oil production

*Paper based on a presentation at POLYCHAR 16: World Forum on Advanced Materials, 17–21 February 2008, Lucknow, India. Other presentations are published in this issue, pp. 389–570.

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operations, such as drilling, cementing, completion, production itself, and treatment of oil and water. Various polymers, oligomers, and macromolecules in general have been evaluated for their efficiency in specific functions. The development of a polymer additive with specific performance generally requires synthesis, characterization, and evaluation of its properties (physical, chemical, and/or physico-chemical), besides application tests.

Based on the experience acquired in synthesis and characterization of copolymers, as well as in studying their physicochemical properties and behavior of their interfaces [1–21], our research group is dedicated to the development of new polymers for application in solution in the petroleum industry. This type of research requires knowledge not only of polymer science, but also of the operations where polymers are applied. For this, the partnership with researchers of the Brazilian Petroleum Company (PETROBRAS) has been a key factor in training our university research team in this area. The knowledge gained about oil operations, allied with the scientific and technological education offered by the Institute of Macromolecules, has permitted a focus on macromolecules applied to the oil and gas sector in the postgraduate courses in polymer science and technology [22].

This article explains the various steps of oil production in which polymers are applied, covering in more detail the research areas being developed and published by our research group on Macromolecules and Colloids in the Petroleum Industry of the Institute of Macromolecules of Rio de Janeiro Federal University. Some recent unpublished results are also presented. We describe the following oil production operations:

- drilling
- cementing
- completion
- production
 - divergence
 - well stimulation (acidizing and fracturing techniques)
 - control of deposits (organic and inorganic)
 - control of hydrates
 - oil recovery
- treatment of oil
- treatment of systems contaminated with oil
- compatibility of polymer additives

It is important to mention that, despite the production of the majority of polymers being a petrochemical process widely used all over the world [23–29], this paper deals with the application of polymer science to the petroleum production.

DRILLING

Drilling of oil wells begins only after analysis of information generated by exploratory research in the prospecting stage, based on geology and geophysics. Drilling entails utilizing means to erode or fracture rocks and to remove the fractured material as the drilling progresses, along with stabilization of the borehole walls and sealing of the well against the entrance of undesired fluids. The rock fragments are removed continuously via a drilling fluid or mud. This fluid is injected into the drilling pipes (drill string) through the rotary swivel and returns to the surface via the annulus (the space between the drill string and borehole wall) [30,31].

Drilling fluid is composed basically of a mixture of water or other base, clay, chemicals, and polymer additives. Its main functions are to carry the fragments of earth and rock being drilled to the surface, maintain the ideal pressure so that the borehole walls do not collapse, maintain a hydrostatic column able to deter the rise of gas and oil, lubricate and cool the drill bit, and reduce friction between the

drill string and borehole wall. Besides this, it must not be harmful to the producing formation, human health, or the environment [32].

Traditionally, drilling muds are classified according to the base used to prepare them, which are air, water, or oil. Most drilling operations in the world use water-based fluids. Nevertheless, these have some disadvantages that can be overcome by the use of oil-based fluids. Currently, a new generation of fluids is under development, formulated with synthetic bases, such as esters, polyalphaolefins, and glycols [32].

Various polymers, such as partially hydrolyzed polyacrylamide (PHPA), vinyl acetate-*co*-maleic anhydride (VAMA), xanthan gum (XG), and carboxymethylcellulose (CMC), are applied in the preparation of drilling fluids to act as thickeners, filter loss reducers, clay swelling inhibitors, drag reduction agents, lubricants, and dispersants [33,34].

The phenomenon of drag reduction in turbulent flows due to the presence of certain flow modifiers has been the subject of many studies in the last few years [35,36]. The investigation of how they work is very important due to their potential application in engineering, since drag reduction of up to 50 % can be obtained through the addition of just a few parts per million by weight of polymeric additives, notably, linear polymers with high molar mass or low fiber concentration [37]. The drag reduction can be manifested as a lower coefficient of friction, a decrease in pressure drop per unit of pipe length, or a reduction in the energy required to pump a fluid or propel an object through a fluid. Water-soluble polymers containing side chains are being studied. Our research group has been studying the preparation and characterization of materials of this nature since 1977 [3,19]. More recently, the performance of these polymers as drag reducers has been evaluated [33].

Owing to the small amount of polymer samples synthesized in laboratories, we had to develop a reduced-scale device to evaluate drag reduction. To do this, we used a steel capillary viscosimeter with a length/diameter (L/D) ratio greater than 115. Since the diameter was approximately 1 mm, this meant choosing a length of 0.41 cm, determined by direct measurement with a tape measure [33]. In more recent studies, we have observed that the insertion of grafts improves the drag reduction performance, as found by other authors [38], but the limitations of content and chain length vary differently in function of the hydrophobicity of the side chain.

Filter loss is the quantity of liquid that enters the well and is absorbed by its walls. The need to reduce this filter loss of drilling fluid is addressed by the addition of polymers with high molar mass, such as pregelatinized starch, or with the use of aphron-containing drilling fluids [39].

Aphrons are a dispersion of gas microbubbles. Once formed, they differ from the bubbles produced in air because they are tough and stable, resisting coalescence into larger bubbles. Aphron dispersions are used in drilling fluids to minimize deep invasion into depleted high-porosity sands while stabilizing shale under pressure. They are composed of two basic elements: a gaseous core and a thin, liquid, multilayered protective shell, sustained by surfactants and a viscosified layer composed of polymers [39]. Our research group has been studying the influence of the composition on the main characteristics of aphrons in water- and synthetic-based drilling fluids. We recently observed the influence of the polymer/surfactant system on the reduction of filter loss of aqueous aphron-based drilling fluids. Fluids that contain XG in their base generate a relatively larger number of aphrons than do fluids containing PHPA as the viscosifying polymer. The use of a copolymer of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) as a surfactant promotes more efficient reduction of filter loss in both water- and synthetic-based drilling fluids. This behavior is correlated with obtaining aphrons with broader bubble size distribution and the fact that the copolymer has an alternating structure of hydrophilic and -phobic groups in the polymeric chain [16].

CEMENTING

When the drilling reaches a certain depth, a steel casing is introduced into the borehole, starting the cementing step. One of the most important factors in this operation is successfully displacing drilling fluid

from the annulus and properly conditioning the annular surfaces to accept and bond with the cement. Primary cementing is the process of placing cement in the annulus between the casing and the formations exposed to the wellbore, excluding the drilling fluid. To achieve this goal, a hydraulic seal must be obtained between the casing and the cement, and between the cement and the formations, while at the same time preventing fluid channels in the cement sheath. The cement provides mechanical support for the casing and prevents the collapse of lines due to pressure [24,35,40].

Additives modify the behavior of the cement system, ideally allowing successful cement slurry placement between the casing and the formation and adequate zonal isolation during the lifetime of the well. The type of slurry used depends on the desired density, the depth of the formation, and its temperature. Filter loss of the slurry is a critical parameter that influences the cement hardening time [25,41].

Polymers are used as additives for various functions. Carboxymethyl-hydroxyethyl cellulose (CMHEC) is used to retard cement hardening; hydroxyethyl cellulose (HEC) with low molar mass and sulfonated polymers are employed as dispersants; and PHPA, polyvinyl pyrrolidone (PVP), and CMHEC act as effective filter loss control agents in cement slurries, even at high temperatures [24,41].

COMPLETION

After the well has been cemented, the communication between the well and the hydrocarbon-bearing formation must be established by perforating the casing and cement (perforation step). Other operations include controlling the production of sand or water and cleaning the well and perforation blockages. During these operations, the well is filled with a fluid compatible with the rock formation, called completion fluid. This fluid's density must be adjusted to promote sufficient hydrostatic pressure to prevent explosions [41].

In the various well completion operations, water-soluble polymers are employed as viscosifying agents and/or to control filter loss of aqueous fluids. The most common are HEC, CMC, guar gum, and XG. The composition of the fluid and conditions to which it is subject will dictate the type of polymer used. High salinity and/or the presence of calcium salts impair the performance of CMC, while under conditions of high filter loss, HEC does not perform adequately.

The production of sand from unstable formations can be a serious problem. The sand plugs the well, reduces productivity, causes erosion of the well walls and inside surfaces of equipment, and creates voids behind the casing, which can lead to collapse of the formation and loss of the well. This sand output can be contained by organic polymers, using the gravel-pack method. The particle-carrying capacity of gravel-pack fluids can be obtained by using XG [42].

PRODUCTION

Since oil is extracted through wells with very small diameters in comparison with the extension of the reservoir, favorable production conditions are necessary so that the oil will flow from the rock formations to the well. These involve the physicochemical properties of the oil, permeable characteristics of the rock, and reservoir thermodynamic conditions of the temperature and pressure. When the energy necessary for production comes from the reservoir itself, it is called primary or natural energy. The recovery of oil using natural pressure is called primary recovery, even if the oil, after reaching the production well, has to be raised to the surface by artificial means [43]. Even in cases where the reservoir conditions are initially favorable to extraction, during the well's lifetime, with the fall in pressure and other interventions that are necessary, some operations are carried out to facilitate the oil flow to the well. The acidizing and hydraulic fracturing techniques facilitate the movement of the oil within the porous rock medium and consequently its access to the well. These two techniques use fluids containing polymers to provide suitable properties for good performance [24]. Injection of water or gas into the reservoir to restore pressure is also utilized. Specifically, the injection of water, with mobility con-

trolled by the addition of polymers, through injection wells is highly efficient by forcing the oil to move toward the production well [44]. During the lifetime of a production well or oil reservoir, various operations are carried out with diverse objectives, from assuring production to preserving equipment and increasing the safety of activities. This category of operations includes those to inhibit/control the formation of deposits (organic and inorganic) [45–47], control the formation of hydrates [48], and inhibit corrosion [49], among others.

The existence of water in the rock formation and the employment of operations involving the use of an aqueous system associated with the shear imposed by the flow of these fluids through the reservoir rock/well/production lines and the presence of amphiphilic molecules, whether they are constituents of the oil itself or added to the system during some intervention, mean the fluid extracted will be a water-in-oil emulsion (w/o). This means the oil must be separated from the water, because the latter contributes to the corrosion of oil lines and equipment and also interferes in refining. The process of breaking down these emulsions is aided by amphiphilic chemical substances, among them oligomers of the polyglycol family [50,51].

The recovery of oil by the water injection technique, which mainly occurs in mature fields, leads to the production of a large amount of water. The produced water (whether from the reservoir or from that injected in operations to boost production) is in the form of an oil-in-water emulsion (o/w), which needs to be treated to remove the oil before it can be reused or discharged in aquifers. This treatment can occur by processes of flocculation/flotation, adsorption, or complexation. In all these cases, the use of polymeric materials—with quite different characteristics due to the different treatment mechanisms—leads to high efficiency [51–55].

A little-explored topic, but one of great economic importance, is the chemical compatibility among the various additives used together in the oil industry. These can interact, causing the formation of undesirable deposits, and can also reduce or increase the efficiency of an additive in the presence of another [56].

Divergence

Hydrocarbon reservoirs often contain layers with different permeability due to natural phenomena or because of invasion of fluids. Therefore, during procedures using injection of fluids in the porous medium where the oil is lodged—such as those involving acidizing, hydraulic fracturing, and scale inhibition—the fluids can migrate preferentially to the most permeable zones, leaving intact those that most need treatment [57]. Thus, it is necessary to do something to induce the treatment fluid to diverge to the low-permeability zones. This is done by obstructing the zones of high permeability through the use of fluids containing additives, called diverting agents [58].

In the majority of applications of the fluid divergence technique, a polymer solution with pseudo-plastic behavior is injected in the reservoir. Few materials can be used under typical reservoir conditions, i.e., with wide variations in temperature, salinity, pH, and others. The polymers that have been used include polyacrylamides with low molar mass, natural polymers such as XG and lignosulfonates, and special polymers developed to tolerate these conditions [59].

The use of viscoelastic surfactants based on aqueous fluid systems is also reported for this purpose, mainly mixed ionics or amphoteric, such as dihydroxyl alkyl glycinate, alkyl betaine, alkyl amide-propyl betaine, and alkylamine mono- or di-propionates, derived from certain waxes, fats, and oils. The surfactant is used together with inorganic salts, organic acids, and organic acid salts or with combinations of these additives.

In this context, there are a large variety of commercial products that can be used with this objective. However, the prepared fluids must have special properties. Therefore, it is fundamental to evaluate these products carefully in advance. In recent studies, we found that amphoteric surfactants, as the amine propionates, have the expected behavior for good performance as diverting agents, maintaining the desired rheological characteristics under the temperature and pH conditions of the reservoir.

Well stimulation

Well stimulation is a set of activities aiming to increase the well's productivity or injectivity. The most common methods used are acidizing (acid or chemical stimulation) and fracturing techniques, which are in turn divided into acid and hydraulic fracturing [30].

Acidizing

Acidizing of a formation consists of the injection of an acid with lower pressure than the formation's fracture pressure gradient, to damage it and increase the well's productivity. HCl is mainly used, but other acids and acid mixtures, such as HCl and HF, are used to dissolve clay or sand. Various chemical additives are employed to minimize the adverse effects and enhance the treatment's efficiency [60].

Water-soluble polymers such as XG, sulphonated polyacrylamide, and even CMC, can be utilized as viscosifying agents. Other polymers invariably present low resistance to the highly acidic medium, undergoing acid hydrolysis during the fluid pumping. While preparing viscosifying fluids, foam formation is common. This can be prevented by the previous addition of polyglycol-based antifoaming agents.

Some of the biggest problems encountered during well stimulation are the formation of acid-in-oil emulsions and the precipitation of asphaltene particles in the acid medium. This can clog the reservoir pores. Mutual surfactants and solvents (e.g., ethylene glycol) are normally added to the acid fluid to minimize such problems [60].

Fracturing techniques

Acid fracturing

In the acid fracturing technique (chemical–mechanical stimulation), an acid solution is injected at a higher pressure than the fracture gradient of the rock formation, causing a pressure fracture. Normally, a pre-flush liquid is injected before the acid to initiate the fracture. A second gellified, aerated, or emulsified acid solution is then pumped into the reservoir to propagate the fracture. This acid solution reacts with the rock formation, creating irregular channels in the fracture faces, through which the hydrocarbon can flow to the well because they remain open even after the fracture closes. Macromolecules, such as CMC and HEC, can also be added to this type of fluid to increase its viscosity [61].

Hydraulic fracturing

In the hydraulic fracturing technique (mechanical stimulation), a fluid is pumped into the rock formation with a sufficient pressure to cause it to rupture by traction, triggering the fracture, which is propagated as the fluid is injected. A granular material is added to the fracturing fluid (proppant or propping agent) to keep the fracture open when the fluid pumping stops, creating a permanent channel for the oil to flow to the well. It is estimated that 40 % of the world's oil wells are stimulated by hydraulic treatment. This is the method used in Brazil in the sandstones of the Campos Basin [61].

Various hydraulic fracturing fluids are available in the market: oil-based fluids, alcohol-based fluids, emulsions, foams, and water-based fluids. Water-based fluids are currently the most commonly used. These fluids are cheaper and not combustible, reducing the risk of accidents. Besides this, their viscosity is easier to control. The performance of water-based fluids regarding transport of the proppant, loss of fluid to the formation, and increase of fracture dimensions is significantly improved by the addition of a polymer with high molar mass, such as guar gum, hydroxypropyl guar (HPG), HEC, carboxymethyl hydroxypropyl guar (CMHPG), and XG [62].

Control of deposit formation (organic and inorganic)

The formation of solid deposits that impair or even prevent the production of petroleum can arise from organic compounds, such as linear paraffins with relatively high molar mass and asphaltenes, or

inorganic ones, such as inorganic salts that are insoluble in the medium. The combined use of incompatible chemical additives can also cause the formation of undesirable sludge deposits.

Organic deposition

Problems related to the crystallization and deposition of heavy organic fractions during the production, transport, and storage of crude oil can cause huge losses to the petroleum industry. The heavy organic fractions can contain waxes, resins, asphaltenes, and organometallic compounds, which exist in oil in different quantities, states, and forms. Problems associated with organic deposition can take place at any stage of the oil production process, from the well to the refinery [46].

Paraffins

The production of oil from deepwater offshore fields presents many serious problems, among them the obstruction of the lines through which the crude oil must flow to the surface, due to paraffin (or wax) deposits. These are formed when the oil comes into contact with cold surfaces ($\sim 6^\circ\text{C}$), particularly prevalent in offshore production. The two parameters usually used to evaluate this phenomenon are the wax appearance temperature (WAT), measured by differential scanning calorimetry (DSC), and the pour point, measured by a special apparatus [63]. The WAT is the temperature at which the process of nucleation and crystallization of *n*-paraffins begins. From this point, the wax crystals formed grow and agglomerate, causing an increase in viscosity, impeding the flow and causing solids deposition. As the temperature decreases even more, the oil temperature can fall below its pour point and stop flowing altogether [64].

One of the most-used techniques to solve the problem of wax deposits involves the use of organic deposition inhibitors (ODIs), which are generally composed of amphiphilic polymeric materials.

The mechanism by which these polymers act occurs during the nucleation step of the first paraffin crystals, provoking the crystal changing in the next step. The symmetric and apolar fraction of the inhibitor molecule attracts, by structural similarity, the paraffin molecules present in the oil, while the inhibitor's asymmetric and polar fraction impedes the growth of the paraffin crystals and thus the formation of large aggregates susceptible to deposition.

Therefore, chemical inhibitors act to modify the paraffin crystals' morphology during the precipitation step and not to prevent their precipitation directly [65].

Our research group has evaluated different polymeric materials, mainly copolymers with different structures. The first additives evaluated were acrylic and methacrylic ester copolymers, synthesized in various compositions: poly(methyl methacrylate-*co*-hexadecyl methacrylate), poly(methyl methacrylate-*co*-octadecyl methacrylate), poly(methyl acrylate-*co*-hexadecyl acrylate), and poly(methyl acrylate-*co*-octadecyl acrylate) [4,7]. We observed that the efficiency of copolymers derived from acrylate was higher than those from methacrylate monomers, probably due to the higher polarity of the acrylic structure than the methacrylic one, which promotes better disarranging of the paraffin crystallization process. As expected, high percentages of hexadecyl acrylate and octadecyl acrylate in the copolymer accentuated pour point reduction, since these chains are similar to the paraffin, increasing the oil/additive compatibility [5].

Other additives were obtained by the reaction of the phosphoric ester (containing long-chain hydrocarbons) with sodium aluminate in solution. These products presented higher efficiency as inhibitors when having a molecular weight within an optimum range and when used at an optimum concentration [66,67].

Among the additives most used to improve the flow of waxy oils at low temperatures are copolymers of ethylene and vinyl acetate (EVA), which are composed of a hydrocarbon chain (apolar) and polar groupings.

We have reported [64,68,69] studies of the effect of EVA on the viscosity and flow of crude oil, varying the concentration of vinyl acetate in the copolymer in increments of 20, 30, 40, and 80 % by mass, and also utilizing different concentrations of this additive. The tests show that the EVA copolymer with highest vinyl acetate concentrations (80 % by mass), although able to modify the crystals,

does not show good efficiency in inhibiting wax deposition. In terms of balance of polar and apolar segments, the other copolymers evaluated were within an optimum range for application as inhibitors. The results obtained with EVAs containing 20 and 30 % vinyl acetate were slightly better than with EVA containing 40 % vinyl acetate. This study also showed that all the copolymers had a strong influence on reducing the viscosity of oil at temperatures below the WAT.

With the aim of extending the use of EVA copolymers to a wider range of oil types, these have been chemically modified by the insertion of long lateral hydrocarbon chains [70–72]. The additives obtained by inserting C12 and C18 chains act to significantly reduce the formation of deposits both in crude oil and its light distillates by reducing the pour point of these fluids. It was also observed that the hydrophilic/lipophilic balance (HLB) of the additive appears to have a more pronounced influence on the performance of copolymers than does molar mass [71,72].

This behavior was confirmed in another work [71], in which polymeric additives based on poly(ethylene-*co*-vinyl acetate) chemically modified by inserting different concentrations of hydrocarbon chains (C14) presented better ODI performance than those obtained by unmodified copolymer. It was concluded that the molecule must retain a hydrophobic/hydrophilic balance in order to keep its capacity to modify the paraffin crystal. This study also showed that copolymers with similar solubility parameters did not have the same pour point values, which suggests that the solubility of the additive is important but is not the only factor that influences the additive's performance. Moreover, the ODI performance is related to its interaction with the paraffin, and as a consequence, to the co-crystallization phenomenon. However, better performance was observed when the additive was already precipitated in the solvent medium at the moment when the wax starts to precipitate.

The influence of petroleum asphalt residue (PAR) [73] on pour point was estimated for solutions of commercial paraffin dissolved in a mixture of solvents. It was shown that some components of the PAR can interact with the wax, so the effect of the competition between the copolymer and the PAR reduces the ODI performance.

The influence of the asphaltenes and naphthenic acids on WAT, pour point, and wax crystallization was evaluated in another work, using the same solvent systems [46]. Asphaltenes reduced the pour point, and this effect increased with rising asphaltene concentrations, indicating that asphaltenes interact with the paraffins to form particles with a different interaction profile. The observation of the wax crystals using optical microscopy revealed, in the absence of additives, a plate- or needle-like structure, whereas when asphaltenes were incorporated the particles were smaller and less well defined. At higher asphaltene concentrations, dark particles whose surface resembled asphaltenes were also observed. Naphthenic acids caused a small increase in the pour point and when fractions, asphaltenes, and naphthenic acids were added together, synergistic effects were not observed.

Recent investigations, using high-pressure differential scanning microcalorimetry (HP μ DSC), have shown that the presence of dissolved gases in and pressure on petroleum (reproducing reservoir conditions) increases the efficiency of the wax deposition inhibitors tested and can serve as a basis to optimize the concentrations of the products to be employed [74].

Asphaltenes

Asphaltenes are the heaviest, most polar, and nonvolatile components of crude oil. This fraction is usually composed of condensed polyaromatic rings containing aliphatic and naphthenic side chains and sulfur, oxygen, and nitrogen as heteroelements or functional groups. Metals such as vanadium and nickel are also present in this fraction as part of porphyrinic or nonporphyrinic groups. Resins are composed of molecules similar to but less aromatic than asphaltenes.

Resins are defined as the fraction of petroleum that is insoluble in ethyl acetate and soluble in hydrocarbons such as pentane, heptane, benzene, and toluene. Asphaltenes are defined as the fraction of petroleum insoluble in light hydrocarbons (pentane, hexane, heptane), but soluble in benzene and toluene. They have molar masses that generally vary from 5×10^2 to 10^3 , but can reach the order of 10^4 .

If obtained by extraction with a solvent, the molar mass of the fraction can vary in function of the alkane chain used as precipitating agent. In general, it is larger the longer this chain is [45].

The interfacial tension measures of asphaltenes in organic solutions, although infrequently mentioned in the literature, were used to calculate the molar mass, by using the slope of the interfacial tension-concentration curves of asphaltenes in nitrobenzene, pyridine, and tetrahydrofuran. The results obtained were lower than those obtained by other methods (308, 766, and 2053 g/mol for nitrobenzene, pyridine, and tetrahydrofuran, respectively), suggesting that the test method was measuring the asphaltene unimers [75].

Owing to their greater polarity, which causes them to be less hydrophobic than other petroleum fractions, asphaltenes have a tendency to agglomerate and may undergo phase separation. Variations in the temperature, pressure, and composition of crude oil during the extraction, transport, and refining stages can compromise the stability of asphaltenes in the oil [76].

There are two main approaches to model this phenomenon. One of these approaches considers crude oil and asphaltic dispersions as lyophilic colloids, and the other considers asphaltenes as intrinsically insoluble components that would be maintained dispersed in the medium by other asphaltic fractions (e.g., resins) [77].

The stabilization of asphaltenes has been studied in model systems, with and without the addition of stabilizers. The asphaltic fraction separates from the petroleum because of the solubility difference when it is dissolved in a good solvent (e.g., toluene or cyclohexane), and its precipitation is induced by the addition of a nonsolvent (e.g., heptane, hexane, or pentane). The stabilization of asphaltenes can be quantified by two methods: (1) the precipitation method, in which the content of asphaltenes that remain soluble in the medium is determined; and (2) the precipitation onset method, in which the volume of flocculating agent necessary to cause the asphaltenes to start precipitating is determined. In both methods, the quantification can be monitored by UV and near-infrared spectrometry at a determined wavelength. These tests performed with and without the addition of a determined concentration of stabilizers revealed the capacity of each additive to keep the asphaltenes stable, even after the variation in the solvent medium's thermodynamic quality [78–82].

Crude oils with low precipitation onsets effectively present instability and depositional problems in field operations, whereas those with a high onset are stable and do not present separation or precipitation in production operations [82]. In another work, it was observed that the origin of the asphaltenes does not play an important role in their onset of precipitation [81].

The precipitation onset of asphaltenes strongly depends on the properties of the nonsolvent used to induce the separation process. For *n*-alkanes, the onset increases and the maximum amount of precipitate decreases as the molar mass of the nonsolvent increases. It is interesting, however, to note that the solubility parameter of the solvent medium at the asphaltene precipitation onset is very similar for the various alkanes considered, and for crude oil lies between 16.6 and 16.9 (MPa)^{1/2} [82].

In our studies, we have also evaluated the precipitation of asphaltenes in toluene mixtures with other solvents and in crude oil, seeking information that may shed some light on the nature of the interaction determining the asphaltene aggregation process. The solubility of asphaltenes in heptane/toluene mixtures was studied at several temperatures. The precipitation of asphaltenes induced by *n*-alkanes was observed to increase with temperature decrease. With respect to this aspect, asphaltenes behave similarly to paraffins or waxes, unlike the behavior of typically polar compounds [83].

Electric charge and potential may represent important factors in the colloidal stability of crude oil and asphaltene dispersions. The electrophoretic mobility of asphaltene particles formed by precipitation induced by addition of *n*-heptane to asphaltene solutions in toluene was measured in water and in non-polar media. Dispersed in water, the particles showed negative electrophoretic mobility, whereas in toluene their mobility was positive. When resins were present in the precipitating medium, coprecipitation of these fractions occurred, indicating an adsorption or binding process of the resins on the nascent asphaltene particles. This interaction, however, did not significantly change the electrophoretic mobility of the asphaltene particles. In contrast with commercial dispersants, resins failed to stabilize

asphaltene dispersions. These results indicate that the descriptions representing asphaltenes as a solid phase intrinsically insoluble in hydrocarbon media dispersed by adsorbed resin molecules do not accurately represent the structure of these fractions [84].

The behavior of mixtures of asphaltenes with aromatic amphiphilic molecules was evaluated, and it was observed that some compounds promote the stabilization of asphaltenes, such as nonylphenol. It was shown that this stabilization is primarily controlled by the polarity of the head group of the amphiphilic compound and by the length of the hydrocarbon tail bound to the aromatic ring. It was also observed that an additional polar side group can increase the capacity of the amphiphilic compound to stabilize asphaltenes. This capacity rose as the acid–base interactions between the two species improved [78,79].

The use of chemical additives based on the liquid extracted from cashew nut shells to avoid the deposition of asphaltenes was evaluated in our studies [80,85]. These compounds contain C15 chains with variable unsaturation degrees, meta-substituted in the aromatic ring. The similarity of these compounds to the structures described as efficient peptizing agents for asphaltenes prompted us to evaluate cashew nut shell liquid (CNSL) and its derivatives, cardanol and polycardanol, synthesized in our laboratory, as asphaltene stabilizing agents. The results confirm that CNSL and cardanol perform comparably to nonylphenol. Polycardanol was not only less efficient than its monomer, it actually increased the precipitation of asphaltenes. This effect may be ascribed to the large number of phenol groups present in the polymer, which may flocculate the asphaltene particles or increase their polarity, reducing their solubility in aliphatic solvents.

Inorganic deposition

Precipitation of barium sulfate (BaSO_4), strontium sulfate (SrSO_4), and calcium sulfate (CaSO_4), and more commonly of calcium carbonate (CaCO_3) and calcium phosphate (CaPO_4) are observed in the oil industry [86,89]. Problems of mineral scaling on equipment surfaces can be resolved with the continuous injection of chemical additives, called scale inhibitors. The prevention of scaling within the well requires more complex treatments, such as use of a squeeze inhibitor, that is, forced injection of an inhibitor within the formation [86].

Previous work has shown that regular scale inhibitor and even specific CaPO_4 scale inhibitors are not very effective in preventing precipitation of CaPO_4 [88]. A. Zach-Maora et. al suggested by thermodynamic calculations the reverse osmosis (RO) recoveries of 80–85 % were feasible with careful control of feed water pH and the use of chemical additives such as scale inhibitors and chelating agents; they also predicted the major minerals of concern to be silica, calcium fluoride, CaCO_3 , and CaPO_4 [89].

The crystallization of scale deposits results from three mutually interacting processes (supersaturation, nucleation, and crystal growth). Chemical additives can influence each of these processes. When adding a polymer as a scale inhibitor, the inorganic salt tends to precipitate together with the polymer, substantially altering the way this crystal grows. The precipitate loses its ability to adhere and can hence be easily removed from the system [90].

A large number of scale inhibitor formulations are commercially available. These formulations contain synthetic polymers, such as poly(sodium acrylate) and poly(sodium vinyl sulfonate), besides polyphosphates, phosphates, organic phosphonates, etc. [86,87]. An additive's efficiency is represented by how much it can retard the precipitation in a given time interval [86].

Our research group has used scale inhibitors to evaluate the performance in relation to the presence of other additives used in the oil industry. The performance evaluation included conducting standardized CaCO_3 precipitation tests using the polymer base of a commercial scale inhibitor, poly(sodium acrylate). In this study, we observed there is an optimal scale inhibitor both for the commercial formulation and the poly(sodium acrylate) solution alone. This means it is not useful to have too many inhibitor molecules in the system. Besides this, we observed that the efficiency of the pure polymer base

was better than that of the commercial formulation, showing the need to adjust the concentration of this formulation's components [47,56].

Control of hydrate formation

In the oil industry, gaseous hydrocarbon hydrates can block pipelines, impairing production. Controlling their formation can be expensive. The hydrates of natural gas are white, crystalline solids with a cellular structure, formed by the interaction of steam and gaseous hydrocarbons in the presence of free water, under high-pressure and low-temperature conditions.

There are three categories of methods to control hydrates: phase balance shift, thermodynamic inhibition, and kinetic inhibition. Deepwater reservoirs require the use of kinetic inhibitors or anti-agglomerants, which inhibit the crystals' growth, both by preventing agglomeration of the nuclei and by creation of many crystallization centers, leading to a suspension of hydrates that can be transported through pipes. These inhibitors are surfactant polymers such as PVP and acrylic polymers, among others [48].

Oil recovery

Some reservoirs present low-efficiency natural mechanisms, retaining large amounts of hydrocarbons after their natural energy is exhausted. Such reservoirs are good candidates for the use of additional recovery processes. The method of secondary recovery, which involves a conventional fluid-injection process, is widely used although it has limited potential. Tertiary, or enhanced oil recovery (EOR), also utilizes injection of fluids, as does secondary recovery, but causes changes in the physicochemical and/or thermodynamic nature of these fluids and in the interactions between them and the reservoir [90,91]. Within the group of chemical EOR methods is the injection of polymer solutions, which work by increasing the viscosity of the injected water (displacement phase) to approximate it to the viscosity of oil (displaced phase). A fluid's mobility (λ) is defined as the ratio between its effective permeability (k) in the reservoir rock and its viscosity (μ). For example, the mobility of oil (displaced fluid) is given by $\lambda_o = k_o/\mu_o$ and of the water (injected fluid) by $\lambda_w = k_w/\mu_w$. The mobility ratio (M) is defined by λ_w/λ_o . The lower the mobility ratio, the easier it is to recover the oil. In this respect, the polymer acts by reducing the water's mobility by two mechanisms: (1) by increasing the viscosity of the aqueous phase, and (2) by reducing the permeability of the reservoir, caused by the adsorption/retention of the polymer in the rock pore mouths [91–93].

Although the injection of polymeric solutions to boost oil recovery is longstanding (dating to the 1960s), the method today faces two challenges to its wider use: (1) the need to develop polymers that are more resistant to salinity than those available today, i.e., with high thickening effect in a saline environment, because of the use of seawater as an injection fluid in offshore fields and environmental regulations prohibiting the use of freshwater for this purpose, and (2) the dimensioning of the slug to be injected, where slug represents a finite quantity of polymer solution with defined concentration and volume.

The main characteristic of the polymer to be utilized in EOR is its solubility in water. Among the water-soluble polymers currently employed in EOR operations in Brazilian fields are polysaccharides and PHPA. The latter is used in 90 % of the field applications because biopolymers still are not available at competitive prices [91,92]. The use of polyacrylamide has evolved to the partially hydrolyzed form because it is possible to maintain the viscosity of relatively high aqueous solutions using molecules with lower molar mass than those of unmodified polyacrylamide, which makes the system less susceptible to degradation by shearing. This characteristic is related to the expansion of the polymer skein (i.e., increased hydrodynamic volume), due to the repulsion of the negative charges introduced in the molecules by the hydrolysis reaction. Although PHPA is widely utilized, its charged structure makes it susceptible to the presence of salts, so it is unsuitable for use in reservoirs with high salinity. In this

respect, various studies have focused on obtaining polymers that are shear-resistant and can maintain their viscosity at the desired values even in the presence of salts [94,95]. Among these systems are the nonionic hydrophobically associated polymers, which give high viscosity to the fluid by aggregation of the molecules: under relatively high shear levels, these aggregates come apart, reducing the viscosity of the fluid, and under low shear levels the aggregates resume forming, restoring the viscosity of the fluid in the porous medium. Because these molecules do not have charges, they do not lose viscosity in the presence of salts. On the contrary, due to the salting out effect, the fluid's viscosity tends to be slightly higher [19,94–97]. These polymers can be introduced as copolymers of polyacrylamide in the main chain with grafts hydrophobic. The reactions to obtain amphiphilic copolymers of this nature can involve processes of polymerization in solution with mixture of solvents [3] or micellar polymerization, which is more effective in the reaction between hydrophilic and hydrophobic segments.

The objective of dimensioning the polymer slug is to define a sufficient quantity to spread throughout the reservoir, thus fulfilling its technical purpose of displacing the oil. Although the principle involved in polymer injection is straightforward and easy to grasp, the method's success in oil fields is directly related to the selection and dimensioning of the polymer slug solution to be injected, which is done semi-empirically, using only information from physical modeling (laboratory flow testing). The ideal would be for this dimensioning to be done using a computational tool (mathematic simulator) specifically for this purpose. Such a tool is under development and validation in field operations by our research group. It considers the main phenomena associated with the displacement of macromolecules under flow, that is, convection, which are: dispersion, physicochemical adsorption, mechanical retention, and inaccessible porous volume. The first two phenomena are common to any product, while the last two are typical of macromolecules, as is the case of the polymers used in EOR [44,98].

OIL TREATMENT

In the oil dehydration process, the use of demulsifying products is essential to coalesce the emulsions formed in the field. All the agents that prevent or break down emulsions have some tendency to be adsorbed at the interfaces, which permits the displacement of the emulsifiers that stabilize the emulsion [50,99]. There are many chemical demulsifiers available for this purpose. The demulsifiers used in the primary processing of petroleum are in most cases surfactants based on block copolymers of PEO/PPO with different EO/PO molar ratios [100].

Many studies of the physicochemical behavior of demulsifying surfactants have been conducted seeking to correlate them with the performance of the demulsification process [11,12,16,17,20,21,51,101–106].

The evaluation of the solubility of PEO/PPO aqueous surfactant solutions is very important because these compounds present phase separation at increasing temperature. The temperature at which this phase separation occurs is known as the cloud point. Below the cloud point, such copolymers can remain in solution, not as unimers, but in the form of aggregates called micelles. The critical micelle concentration (CMC) and the critical micelle temperature (CMT) are the concentration and temperature at which the micelles start forming, respectively [106].

Our research group has studied several PEO/PPO block-based copolymers: bifunctional triblock copolymers (HO/PEO/PPO/PEO/OH); monofunctional diblock copolymers (R/PEO/PPO/OH and R/PPO/PEO/OH, where R length is linear C_4 and C_{12}) [3,20,22]; and star PEO/PPO block copolymers, designed as tetronic polyols [3,20,22,46,68]. We observed that the physicochemical properties (cloud point, CMC, and CMT) depend on the EO/PO ratio, polarity, R length and position of the hydrophilic (EO and OH) and hydrophobic (C_4 or C_{12} and PO) segments along the molecule. The copolymers in which hydrophilic/hydrophobic segments are adjacent present lower CMC values, independent of EO/PO ratio. Such behavior was attributed to the ease of molecular association induced by the structure of the copolymer in which the hydrophilic/hydrophobic segments are adjacent [11,16,17,103]. The

higher the EO/PO ratio in the copolymers, the higher the oxidative thermal stability of PEO/PPO mono-functional block copolymers [21].

One of the strategies studied to minimize the reduction of surfactant solubility in aqueous solution is the addition of hydrotropes [107]. We have used sodium *p*-toluene sulfonate (NaPTS) [12,17,18,20,103,105] and butyl monoglycol sodium sulfonate (NaBMGS), and observed that the increase of system solubility closely depends on the composition, structure, and the hydrocarbon chain length present in the copolymer molecules [108].

The interactions of the hydrotrope NaPTS and the copolymer PEO/PPO were studied by hydrogen and carbon-13 NMR spectroscopy. The nonaggregated NaPTS did not present interaction preference with the copolymer in the unimeric or micellar form. On the other hand, aggregated NaPTS had a less intense interaction with the copolymer in the micellar form, suggesting that only the copolymer molecules free in solution are able to penetrate the organized NaPTS network [12].

By analyzing the performance of aqueous PEO/PPO solutions and their mixtures as demulsifiers, we observed that the best efficiency was achieved by the PEO/PPO star structure, which has the hydrophilic segments (PEO and OH) side by side at the free end of the molecule. However, they cost more than linear molecules. This copolymer also exhibited the highest water solubility. Such behavior was attributed to its structure, which promotes a better interaction with the water droplets that are dispersed in the w/o emulsion. It is possible to add up to 30 % of a poor-performing demulsifier to a good one and still get good performance of the demulsification process, reducing its cost [51].

Despite the efforts dedicated to studying the physicochemical behavior of surfactants in solution, it is still not possible to establish direct relations with the demulsifying performance. Among the relations established, it has been observed in studies using Campos Basin (Brazil) crude oil and chemiometry techniques that density, viscosity, surface tension, and nickel content influence the oil separation. Density, pour point, WAT, and nitrogen content are the properties that influence the diameter of the emulsion drops [104].

Sjöblom et al. [109], in the review work, showed that in order to understand the complex picture behind water-in-crude oil emulsion stability, a thorough knowledge at both ambient and high pressures should involve the structure and properties of the crude oil components (mainly the heavy ones), their association tendencies and accumulation at w/o interfaces, their solubility and sensitivity toward changes in pressure and temperature, and others factors.

In recent studies by our group, we observed that one of the main factors that interferes in the demulsifying process, and consequently in demulsifier performance, is the type and state of aggregation of the surfactant present at the interface to stabilize the w/o emulsion.

TREATMENT OF SYSTEMS CONTAMINATED WITH PETROLEUM

Water

The water produced contains a series of organic and inorganic components that must be removed before this water can be re-injected in the well or discharged into the ocean without having a negative environmental impact. The organic compounds can be divided into four groups: aliphatic, aromatic, and polar compounds and organic acids [110]. The aliphatic compounds consist of the free oil, with low solubility in water. The aromatic compounds, such as benzene, toluene, ethyl-benzene, xylene (BTEX), and naphthalene, are relatively soluble in water. This medium also contains polyaromatic hydrocarbons (HPAs) with high molar mass. Heavy metals, such as lead, nickel, chrome, zinc, copper, and silver, also can be found in the produced water [111].

Various processes are available to treat the oily water produced. These can be classified into three types: primary separation, where hydrocyclones, washing tanks and degasification devices are used; secondary separation, with the use of induced gas flotation (IGF) and chemical additives; and tertiary

separation, which includes the use of centrifuges, activated charcoal filters, membrane filters, and additives for bioremediation [112].

The processes using copolymers for water treatment can be divided into three mechanisms: flocculation, adsorption, and complexation.

Flocculation

The process of separating oil from water by means of breaking the o/w emulsions can be done by flocculation, in which polymers are widely applied. The products generally recommended are cationic polyelectrolytes, but their use in the petroleum industry is limited [113].

Interest in the study of nonionic polymers has been growing, particularly of water-soluble amphiphilic polymers. Studies in this area have focused on the synthesis and evaluation of the properties in solution of modified polymers, which are characterized mainly by their interfacial activity [114].

In this area, one of the first works carried out by our group was to synthesize terpolymers based on vinyl acetate, vinyl alcohol, and graft chains (C12 or C18), presenting different HLBs. Low incorporation levels of the hydrophobic segment are sufficient to promote a significant variation in solubility, making the new material insoluble in water at room temperature. Smaller hydrophobic segments (C12), distributed along the chain, promote greater modification of the material's solubility in organic solvents. There is no variation in the surface tension of modified polymers that are still soluble at room temperature in relation to 80 % hydrolyzed poly(vinyl alcohol) (PVA) [114].

In other experiments, we incorporated carbamate groups in the partially hydrolyzed PVA, besides hydrocarbon chains (C12 and C18), generating polymers presenting different HLB values. As expected, there was a variation in the compounds' solubility, due to the inter- and intramolecular interactions. Besides this, some molecules showed greater resistance to the saline medium. The best flocculant performances were obtained with polymers with relative low molar mass of 70 000, functionalized with C18 chains and carbamation time of 180 min. The optimal concentration was around 5 mg/L. In general, the efficiency of the process appeared to regress with increasing urethane content in the medium [53,113].

Studies with commercial nonionic polymers, based on PVA, PEO, and ethylene oxide and propylene oxide copolymers (PEO/PPO), presenting different structures and HLB values, showed that 5 mg/L of PVA-based solutions were capable of achieving an efficiency rate of ~92 %, while linear PEO/PPO-based copolymers attained similar performance (87.7 %) only at higher concentrations (10 mg/L) [105].

For PEO/PPO-based additives, the molecule having the strongest hydrophilic character had better performance in view of its higher mobility in the dispersing medium. For these copolymers, the chemical structure and HLB were the two factors most strongly influencing the performance of flocculating agents. However, for additives based on homopolymers (PVA and PEO), the additive efficiency rises with the increase in molar mass. The choice of the additive in terms of structure, composition, molecular weight, and HBL depended on the composition and concentration of oily water to be treated, with lower contents of oil in water requiring more hydrophilic additives [105]. The aggregation status of the systems was evaluated in a photometric dispersion analyzer (PDA), which permitted quickly and easily determining the optimal dosage of each flocculating agent in the medium [115].

Adsorption

Adsorption is a process by which the molecules of a solute pass through a microcrystalline or resinous sorbent, remaining fixed at these sites due to the action of physical forces (physical adsorption) or of chemical bonds (chemical adsorption) [116].

Traditionally activated charcoal has been used to treat drinking water and wastewater. Although activated charcoal has been shown to be an effective adsorbent of some organic compounds, the adsorption bond between the functional groups at the surface and some organic species is so strong that the desorption process is difficult and incomplete, limiting its use in some cases [117].

Macroreticulated polymeric resins have been employed as an alternative adsorbent to remove specific organic compounds. These resins can (reversibly) adsorb organic compounds from solutions or

suspensions, minimizing the difficulty of desorption because of the type of bond formed between the organic compounds and the resin surface [118].

In the oil industry, polymeric materials have been tested as column fillers, where emulsions with total oil and grease content (TOG) between 20 and 50 mg/L were reduced to levels between 5 and 20 mg/L after treatment of ~100 bed volumes [119].

Our research group has conducted studies of polymeric resins seeking to reduce the TOG of water extracted from oil wells to the lowest possible level, besides evaluating specific components, such as BTEX and HPA. We synthesized and characterized polymeric resins based on vinyl and acrylic monomers and generated spherical and porous materials through the polymerization in semi-suspension technique, varying the composition and ratio of the diluents [6].

The porous structure of the spheres produced was very diversified, ranging from highly gel-like structures to macroporous ones with surface areas greater than 440 m²/g and pore volumes near 0.70 cm³/g [6]. New resins were evaluated for performance in treating oily water. In this effort, in a first study, the resins were packed in steel columns measuring 20 × 0.78 cm (height × diameter) and their characteristics were tested after elution of about 1900 mL of synthetic oily water with concentrations ranging from 50 to 150 mg/L of oil. The factor that had the greatest influence on the performance was the morphology of the polymer's beads. Better results were obtained with more reticulated structures with smaller pores [54,120]. In terms of chemical structure, the best results (84.8 % efficiency) were obtained with resins of divinylbenzene previously swollen in ethanol. The preparation of columns packed with two or more types of resins, with different hydrophilic character, increased the system's efficiency (89 %), confirming that different compositions of resins in the column retain different substances in the water produced [54,120].

In later studies, focusing on the elution process, we selected the mixed column containing polymeric resins with specific areas of 646 and 70 m²/g. The columns were evaluated at a flow rate ranging from 5 to 50 mL/min of synthetic oily water prepared in advance, with fresh columns being used for each of the flows studied. The contaminant removal percentages were quite high at all the flows tested (>97 %), but the maximum retention rate was attained at a flow of 7.0 mL/min, which was considered the optimal flow. The evaluation of resins submitted to relatively high pressures showed that they have adequate mechanical resistance to this process.

The process of saturation conducted at 7 mL/min with synthetic emulsions (TOG = 200 mg/L) revealed high efficiency (~100 %); only after elution of 102 000 mL (corresponding to 11 087 times the bed volume) were the maximum discharge values permitted by law attained (29 mg/L) [121]. Column regeneration studies were carried out with elution of a solvent mixture of ethanol/hexane at a proportion of 30/70.

Recently, we evaluated the resaturation process, in which nearly 3646 times the bed volume was eluded (~35 000 mL), where the concentration measured remained at zero. After this point, the saturation process was started with TOG values in the range of 10–150 mg/L. This reflects the fact it is possible to regenerate the material for new cycles of use, but that the pair of solvents utilized may not have been efficient for the complete desorption of the contaminants [122].

The success achieved in bench studies prompted our research group to develop a scaled-up project using columns of 80 × 2.94 cm (height × diameter). The mean efficiency was 97.2 %. So far we have treated volumes of oily water (50 mg/L of oil) in this set-up of 4572 times the bed volume. We have also tested the retention of BTEX and HPA in this same system and obtained respective efficiencies of 95 and 99 %. These results demonstrate the efficiency of the process on an industrial scale, with removal of a wide range of toxic compounds present in the water produced by the oil industry.

The use of organophilic clay-based materials associated with primary and secondary oil removal methods showed high efficiency of the water treatment process, with only 0.1 mg/L detected in the treated effluent [123]. Our group has also been studying polymers incorporated with organophilic clays in an attempt to obtain materials to treat oily waters [124].

Complexation

The main problem related to the presence of heavy metals in the water produced by the oil industry is due to their capacity for bioaccumulation in the food chain.

Complex polymer-ion systems have important applications in environmental chemistry, such as the complexation of PVA with Cu(II) ions from the hydroxyl groups, at pH levels greater than 6 [55].

The removal of the Zn(II) ion from solutions was studied through their complexation with a series of poly(acrylamide-*co*-acrylic acid) copolymers, as well as their homopolymers based on acrylamide and acrylic acid. It was observed that an increase in the acrylic acid content in the copolymer generated a stronger complexing interaction with Zn(II), reaching a degree of efficiency of 88.2 % in the case of the homopolymer based on acrylic acid. These results show that the copolymer's acid group has stronger interaction with the metal than the amide group. Tests also showed that an increasing concentration of complexing material in the contaminated solution helps enhance the solution's decontamination efficiency [125].

Sand and other

The surface soil layer can be contaminated by organic compounds, especially chlorinated solvents, petroleum, and its derivatives, as a consequence of accidental spills and leaks from pipelines and storage tanks. Heavy investments have been directed to research and development of new technologies that can be applied to the clean-up of contaminated soils, including the study of possible changes in operating principles and process variables.

In recent years, surfactant products have been used to clean up soils and aquifers contaminated by hydrocarbons or other petroleum derivatives. However, these systems have a tendency to form macroemulsions and gels or liquid crystals. Macroemulsions are thermodynamically unstable, and due to the relatively large size of the droplets, between 0.1 and 10 μm , they tend to clog the pores during their transport in the soil, impairing the cleaning process [126].

The performance of microemulsions as an alternative process for remediation of areas contaminated by organic compounds, particularly the heavy fractions of petroleum, is thus being evaluated [127].

Microemulsions are transparent and thermodynamically stable systems containing portions of oil and water stabilized by amphiphilic compounds (surfactants and cosurfactants). The main factors that limit the employment of this technique at greater scale are related to the toxicity of the products used, the costs and the recovery of the contaminant [128].

Microemulsions were obtained, characterized, and evaluated for their potential application in removing hydrocarbons in surface and underground soils and residues of the oil industry. Oil-in-water microemulsions were prepared with a nonionic surfactant and different cosurfactants using as the oil phase a hydrocarbon mixture of linear, cyclic, and aromatic hydrocarbons. This organic mixture ensures the solubilization of the crude oil heavy fraction, such as asphaltenes and resins, which are insoluble in normal aliphatic solvents. The results indicate that the addition of hydrotropes causes a reduction in the minimum amount of surfactant and cosurfactant necessary for the solubilization of the oil phase. When samples of sand contaminated with asphaltene residues were treated with these microemulsions, it was observed that the oil fraction was incorporated in the organic phase of the dispersion and that the contaminant was almost totally removed. These studies are being extended, aiming at the development alternative techniques to remove oil from soils contaminated with organic compounds [127].

Recently, we have begun a study of the application of nanoemulsions for cleaning up contaminated soils. Unlike microemulsions, nanoemulsions are not thermodynamically stable and their formation depends on the temperature, pressure, composition, and experimental procedures used to prepare them.

Some authors have indicated that although not essentially necessary, nanoemulsions can be produced using mixtures of surfactants without any other type of interfacial agent (cosurfactants and hydrotropes). The masses of oil and water utilized in the process are very near, while the quantity of surfac-

tant is in the range of 3–10 % of the total mass of the mixture [129]. This permits large volumes of emulsions to be made with few materials, since a nanoemulsion also maintains its particle size even under great dilution.

Nanoemulsions of orange oil/water were prepared recently in our laboratories using a high-pressure homogenizer, in the presence of surfactant mixtures based on ethoxylated lauryl esters. These nanoemulsions, prepared at pressures of 17 500 psi for three cycles, were tested to clean sand contaminated with crude oil. The results were compared with those obtained using a macroemulsion of orange oil/water to clean this same contaminated material. All the cleaning solutions were left in a shaker bath for 1 h and the quantification of the sand cleaning efficiency was by extracting the oil from the sand after treatment. The results showed that the nanoemulsion reached a cleaning efficiency above 98 %, while the macroemulsion was below 95 %.

OTHER APPLICATIONS

Other polymer-based additives, such as corrosion inhibitors and antifoaming agents, are used in more than one petroleum industry operation.

Problems related to corrosion arise on the metal surface of tanks, pipes, and other equipment due to the aggression of liquids (oil containing water and hydrogen sulfide, CO₂, formation water, or seawater). Various alternatives are being studied and applied to fight corrosion in oil fields, among them cathodic protection, coatings, corrosion inhibitors, etc. [130]. Many studies have presented amines as efficient corrosion inhibitors on metals, from primary amines to quaternary ammonium salts. However, it has been reported that polymeric compounds are more efficient as corrosion inhibitors. Among these are surfactants of the aliphatic amino polyester family. The inhibition is attributed to the adsorption of the surfactant molecules onto reactive sites on the metal surface, preventing supply of the aggressive ions to the surface and/or transport of reaction products away from the surface [48].

In oilfields, gravitational separator vessels are used to remove the emulsifying agents present at the interface of phases and to permit the coalescence of water droplets, which are associated with the pumped crude oil. Although there are many factors that influence the performance of these separators, the crucial problem is foaming, which hinders the mechanical control of the liquid level, taking up too much space in the separation vessels and reducing their capacity and efficiency. For this reason, anti-foaming agents are added. The most widely used polymer for controlling foaming of crude oil in gravitational separators is silicone, normally together with hydrophobic particles [131]. However, other studies have been conducted with polyester silicones, that is, silicones grafted with chains of PEO and PPO to enhance efficiency and/or reduce costs.

COMPATIBILITY OF POLYMERIC ADDITIVES

Chemical additives are used to combat various operational problems, such as corrosion, scaling, foaming, formation of emulsions, etc. However, the efficiency of the chemical additives tested individually in specific performance tests may not be reproduced when they are part of a cocktail of additives in the production fluids [132].

Synergistic effects can occur when chemical additives are used in admixtures in the petroleum industry. Such effects can enhance or diminish the performance of each additive and/or can cause undesirable residue. The knowledge of these kinds of effects permits (1) optimizing the amount of each additive added, (2) preventing damages, and (3) reducing residue disposal.

In mature oilfields, the injection of seawater and/or re-injection of produced water for secondary recovery is a common practice, increasing the quantity of additives used in oil production operations. The reason is that both the injection water and the fluids produced with higher water/oil ratios need considerable quantities of additives in the production line. In this case, scale inhibitors, demulsifiers, and flocculants are used simultaneously [132].

Little is known about the interactions of these additives, that is, about the synergistic effects of mixtures of chemical additives used in oil production, mainly in the oil/water separation process. To enhance the separation efficiency, chemical additives such as demulsifiers and antifoaming agents are injected into the fluid before it goes to the separators. Besides this, corrosion inhibitors are also used to protect the metal surfaces of pipes and vessels. There is no information available on to what extent these additives can be contributing to the formation of stable emulsions, or on whether the performance of demulsifiers and antifoaming agents are affected by simultaneous use [132,133].

The effects of interactions of demulsifiers, antifoaming agents, and corrosion and scale inhibitors on the stability of emulsions have been studied. To do this, measures of the interfacial tension, surface film pressure, and emulsion stability have been conducted through conventional bottle tests, using synthetic emulsions with kerosene as the oily phase. Negative synergistic effects were observed of mixtures of demulsifiers and corrosion inhibitors, which significantly increase the stability of the emulsions. In contrast, combinations of antifoaming agents and scale inhibitors had little influence on the stability of these emulsions [132,133].

We have evaluated the influence of polymeric bases on the synergistic effects that occur when some additives (demulsifiers, flocculants, and scale inhibitors) are used in admixtures in the petroleum industry. The polymeric bases used were a block copolymer of poly(ethylene oxide-*b*-propylene oxide) as a demulsifier base, a cationic polyacrylamide as flocculant base, and a poly(sodium acrylate) as a scale inhibitor base. After physical characterization of the polymeric bases, we conducted specific performance tests with each additive individually and with their binary and ternary mixtures. In addition to this, we ran gravimetric tests to evaluate the solubility of additives, using produced oily water, to verify the formation of sludge [47,56].

Regarding residue formation as well as the specific performance of each additive, polymeric bases are at least in part responsible for the synergistic effects shown by commercial additives. The polymeric base is responsible for the positive synergistic effect occurring in the presence of the flocculant and/or the scale inhibitor on the demulsifier performance, as well as for the negative synergistic effect occurring because of the presence of a demulsifier and the mixture of demulsifier and flocculant on the performance of the scale inhibitor. Furthermore, it is also responsible for the lower residue formation observed in the flocculant and scale inhibitor mixture, which is a positive synergistic effect [47,55].

ACKNOWLEDGMENTS

We thank the Coordinating Office for Improvement of University Researchers (CAPES), the National Council for Scientific and Technological Research (CNPq), the Office of Finance Studies and Projects (FINEP), the National Petroleum Agency (ANP), and Petrobras Research Center (CENPES) for financial support.

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