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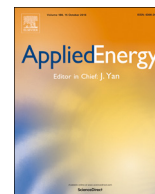
Chemical enhanced oil recovery and the role of chemical product design

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HIGHLIGHTS

- An in-depth review of Chemical Enhanced Oil Recovery methods is presented.
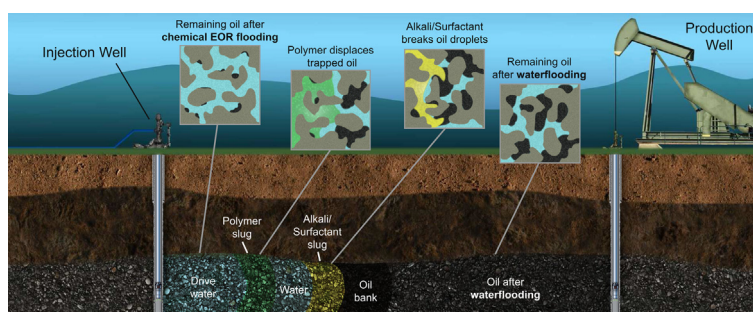- Polymers increase macro-/microscopic recoveries due their molecular interactions.
- Polymeric surfactants enhance both viscoelastic and interfacial properties.
- The chemicals' synergy in combined processes contributes to increase the recovery.
- The architecture of the chemical agents plays a key role in the recovery process.

GRAPHICAL ABSTRACT

ABSTRACT

The current and prospective worldwide energy demands have led either to start exploiting the more difficult and costly unconventional oil reserves, or to maximize the exploitation of conventional oil sources. This triggered the development of enhanced oil recovery processes in order to improve the efficiency and lifetime of mature oilfields. Chemical Enhanced Oil Recovery is one of the most interesting group of methods nowadays. The use of chemical products such as polymers, surfactants, alkalis and polymeric surfactants has been continuously increasing during the last decades. However, these chemicals should be designed to withstand the harsh conditions present in the reservoir (e.g., dissolved salts, pH, temperature, presence of bacteria) and increase the efficiency of the process. One of the key factors in this development is the (macro)molecules' architecture and its influence on the physical properties of the fluids being injected: from linear to branched polymers, from monomeric to gemini surfactants. Furthermore, the combination of these chemicals has showed a great potential due to the synergy between them, creating a new spectrum of techniques in chemical Enhanced Oil Recovery. This review presents the work done in this field with an analysis of the products and technologies employed, including their limitations and possible ways to improve their performance. All in all, the need of advanced products for oil recovery and new, or improved, energy sources has set off a new field of research wherein chemical product engineering plays a major role.

1. Introduction

It is undeniable that oil has changed radically how society lives and how the economy works as any other energy source in the past has ever done. The changes generated in both the society and economy over the last 200 years are more than obvious [1], since the demand for energy began to increase sharply along with the population growth and industrial activity [2]. From that moment on, oil consumption has been

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Nomenclature

AA	Acrylic Acid
AA-Na	Sodium Acrylate
AM	Acrylamide
AMPS	2-acrylamide-2-methylpropane sulfonic acid
API	American Petroleum Institute
APS	Alkaline/Polymeric Surfactant Flooding
ASP	Alkaline/Surfactant/Polymer Flooding
ATBS	Acrylamide-tertiary-butyl sulfonate
ATP	Adenosine triphosphate coenzyme
ATRP	Controlled Atomic Transfer Radical Polymerization
Bbl	Oil Barrel (approximately 0.159 m^3)
BHMPAM	Branched hydrophobically modified polyacrylamide
BHPMP	Bis-Hexamethylene Triamine-Penta (Methylene Phosphonic)
c$*$	Overlapping Concentration
CAC	Critical Aggregation Concentration
CATIN	Cationic Inulin
CDC	Capillary Desaturation Curve
CDG	Colloidal Dispersion Gel
CMC	Critical Micelle Concentration
CMI	Carboxymethylinulin
CTL	Coal to Liquids Technology
De	Deborah Number
DETPMP	Diethylenetriaminepenta (Methylene Phosphonic Acid)
DPEA	Dodecyl Polyoxyethylene Acrylate
DPR	Disproportionate Permeability Reduction
EA	Ethyl-Acrylate
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
FAWAG	Foam Assisted Water Alternating Gas Flooding
FENE	Finitely-Extensible Nonlinear Elastic
GTL	Gas-to-Liquids Technology
HAPAM	Hydrophobically modified associating polyacrylamide
HASE	Alkali-swellable emulsion
HDTMP	Hexamethylene Diamine-Tetra (Methylene Phosphonic) Acid
HEUR	Ethoxylated Urethane
HMBHAP	Partially Hydrolyzed Microblock Hydrophobically Associating Polyacrylamide
HMHEC	Hydroxyethylcellulose
HMPAM	Hydrophobically Modified Polyacrylamide
HPAM	Hydrolyzed Polyacrylamide
IAPV	Inaccessible Pore Volume
IEA	International Energy Agency
IFT	Interfacial Tension
IOR	Improved Oil Recovery
K	Absolute Permeability
K_{MH}	Mark-Houwink Parameter
k_r	Relative Permeability
LPS	Linked Polymer Solution
M	Mobility Ratio
M_w	Molecular Weight
MAA	Methacrylic Acid
MENA	Middle East and North Africa region
MTOE	Million Tons of Oil Equivalent
n	Power Law Exponent
n_2	UVM Parameter
N_{vc}	Capillary Number
NNDAM	N,N-dimethyl acrylamide
NVPMTOE	N-Ethenyl-2-pyrrolidone

OOIP	Original Oil in Place
p	Pressure
P^d	Brooks -Corey Capillary Pressure Parameter
PAA	Poly-(Acrylic Acid)
PAG	Polymer Alternating Gas Flooding
PAM	Polyacrylamide
PASP	Polyaspartates
PEO	Poly-(Ethylene Oxide)
PMES	Polymeric methyl ester sulfonate
PNP	Polymer Coated Nanoparticles
ppb	Parts per Billion
PPCAP	Poly Phosphino Carboxylic Acid
ppm	Parts per Million
PVP	Polyvinylpyrrolidone
RAFT	Reversible Addition-Fragmentation chain-Transfer Polymerization
RF	Oil Recovery Factor
RPM	Relative Permeability Modification
S	Phase Saturation
SAG	Surfactant Alternating Gas Flooding
SDS	Sodium Dodecyl Sulfate
SG	Specific Gravity
SRB	Sulfate Reducing Bacteria
TBA	N-(1,1,3,3-tetramethyl butyl) Acrylamide
TDS	Total Dissolved Solids
UVM	Unified Viscosity Model
v	Darcy Velocity
WEO	World Energy Outlook

Greek letters

α	dynamic capillary pressure parameter
α_{MH}	Mark-Houwink parameter
$\dot{\gamma}$	shear rate
η	intrinsic viscosity
λ	Brooks-Corey capillary pressure parameter
λ_2	UVM parameter
λ_w, λ_o	phase mobilities
μ	dynamic viscosity
μ_{MAX}	UVM parameter
ρ	fluid density
σ_{ow}	interfacial tension of the water-oil system
τ	dynamic capillary pressure coefficient
τ_2	UVM parameter
τ_r	critical shear rate (Carreau model)
ϕ	rock formation porosity

Superscripts

dyn	dynamic
qs	quasi-static

Subscripts

a	aqueous phase
c	capillary
L	lower Carreau viscosity
nw	non-wetting phase
o	Oleous phase
r	residual
U	upper Carreau viscosity
w	wetting phase

steadily increasing to become, during the twentieth and the first decade of the twenty-first centuries, the most utilized energy source. The direct consequence of this is that the global economy depends heavily on these resources. This escalation in the demand originated an era of progress in the exploration and exploitation of new oilfields as well as in the oil refining processes [3,4].

This review focuses on the analysis of different chemical enhanced oil recovery techniques, discussing the chemical products used, and how these can be optimized in order to increase the efficiency of current conventional oilfields. Section 1 presents background information about the present and prospective energy situation and the different stages/mechanisms in oil recovery. In Section 2 we introduce the concept of enhanced oil recovery and how its different methods can increase the performance in mature oilfields. Subsequently, in Sections 3–5 we analyze the main products used in chemical enhanced oil recovery, discussing over the corresponding mechanisms, the desired properties for recovery processes and how these can be optimized by altering the molecules' architecture, hence optimizing the use of existing energy sources. Section 6 presents the combination of the mentioned chemicals and how the synergy of these acting together can further increase the recovery factor in the rock formation. Finally, in Section 7 we present the conclusions about our study, setting future research points in which product design will play a major role.

1.1. General considerations and energy situation

Oil is a fossil fuel, composed essentially by organic substances that undergo chemical and thermal processes for long periods of time (in the order of several millions of years), migrating firstly and then being trapped into porous media formations, called "reservoirs" [5]. It is a non-renewable energy source based on the fact that, although each year petroleum is generated due to the mentioned processes, the generation rate (estimated at a few million barrels per year) was widely surpassed long ago by the annual world consumption (e.g., during 2014 this value was roughly 32×10^{12} barrels) [3,6]. As obvious conclusion from this reality, many authors have speculated about the capability of a non-renewable source to supply a constantly growing demand. Hubbert's [7] initial theory of "peak oil" predicted an increase in oil production until reaching a peak and then a steady decline until the full depletion of economically exploitable oil resources. This model was later improved when other parameters were taken into account, such as the current production capacity, the increase in consumption, the discovery of new exploitable reserves and the development of new technologies [8–16].

Different oils can be primarily classified according to their API gravity, calculated using Eq. (1.1), and their dynamic viscosity (Table 1) [17].

$$API\ gravity = \frac{141.5}{SG} - 131.5 \tag{1.1}$$

It is generally considered that currently the first two types (light and medium oils) are what is known as "conventional oil", whilst the others belong to the category of "unconventional oil" [18]. As of 2014, the current proven reserves and resources for the different types of oil (this means, reserves that have a 90% chance of exploitation) are presented in Fig. 1[3,19,10].

Currently oil is the most used energy source in the world supplying 33% of the total demand. In the period 2015–2035 an increase of 38% in the total energy required can be forecast, associated with the population growth and development of the global economy. In this scenario oil will continue to occupy, although to a lesser extent, the first place by supplying 27.4% of the total (Fig. 2) [3]. This implies an increase in the production of almost 15% in the next years in order to comply with the future energetic requirements (provided that current energy policies remain in force).

As a conclusion, it is obvious that the world economy is not ready to

stop relying on oil. This fact is also supported on the evidence that newer, cleaner sources of energy (e.g., wind, solar, fuel cells) are not ready to take a step forward and replace oil as the main source for the world's demands [14,15]. This scenario is further complicated by the general estimation that in the near future there will be no more significant discoveries of conventional oilfields [13–16]. This implies two possible outcomes: either start exploiting unconventional oil sources, with the immediate consequence of the increase in the price of refined products, or make a better use of conventional oil reservoirs. The objective in Enhanced Oil Recovery (EOR) is to develop the second strategy, i.e., developing new and more efficient methods in order to improve the recovery of the oil still trapped in the fields.

The International Energy Agency (IEA) in its World Energy Outlook (WEO) has forecast a significant increase in the oil production by means of both EOR methods and non-conventional sources during the next 15 years (Fig. 3). The upsurge of these processes will be inevitably coupled to an increase in the price of crude oil, which has showed, even with some ups-and-downs due to economy fluctuations/crisis (e.g., the 2008 World Crisis), a steady upward trend (Fig. 4).

1.2. Oil recovery mechanisms

Throughout the operation period of an oilfield three different stages can be distinguished, corresponding to particular physical production mechanisms. The first stage (primary recovery) is based on the production of oil by natural drive-mechanisms and, later on, by means of pumping devices (e.g., pumpjacks) until the pressure inside the well is no longer enough to render the operation profitable. This production stage is performed with no injection whatsoever of displacing fluids into the reservoir [23–25]. At the end of primary recovery an estimate ranging from 10 to 25% of original oil in place (OOIP) can be recovered [23,24,26,27]. After the primary recovery is considered no longer economically profitable, the secondary recovery takes place. A fluid (water or an immiscible gas) is injected in order to re-pressurize the rock formation and act as a displacing agent pushing oil from injectors to producers. As time passes on, the water begins to come out in the producing wells (water breakthrough) and hereinafter the percentage of produced water (water-cut) increases. It has been reported that some wells remain economically operational with water-cuts as high as 99% [26]. At the end of economic life of the secondary recovery, generally an additional quota ranging from 15 to 25% of the OOIP can be recovered [23,25,26,28]. These two recovery stages can then account for 50/55% of the OOIP. It is at this moment when the tertiary stage or EOR begins. In most cases, secondary recovery and EOR stages begin long before the economic limits are reached (Fig. 5). This is formally considered as a subgroup of what is known as Improved Oil Recovery (IOR). This comprises, besides EOR, all the advanced oil recovery techniques employed in any of the three stages of production of a reservoir to increase the oil recovery [24,29,30]. Some examples of IOR methods are, among others: hydraulic fracturing, scale-inhibition treatments, horizontal wells, acid stimulation procedures, new drilling and well technologies, and advanced reservoir monitoring techniques.

Table 1
General oil classification according to their physical properties.

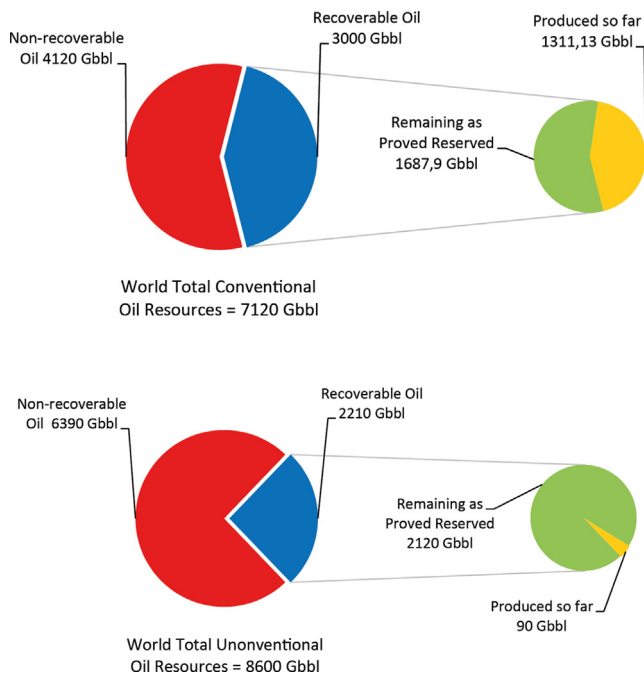| Oil Classification	API Gravity degr API	Dynamic Viscosity cP
Light oils	>31.1	<100 cP
Medium oils	22.3 < °API < 31.1	<100 cP
Heavy oils	10 < °API < 22.3	>100 cP
Extra-heavy oils	< 10	< 10000 cP
Natural bitumen (or tar sands)	< 10	> 10000 cP

Fig. 1. Conventional (top) and unconventional (bottom) oil resources expressed in (Giga) barrels (adapted from BP [3] and OECD/IEA [20]).
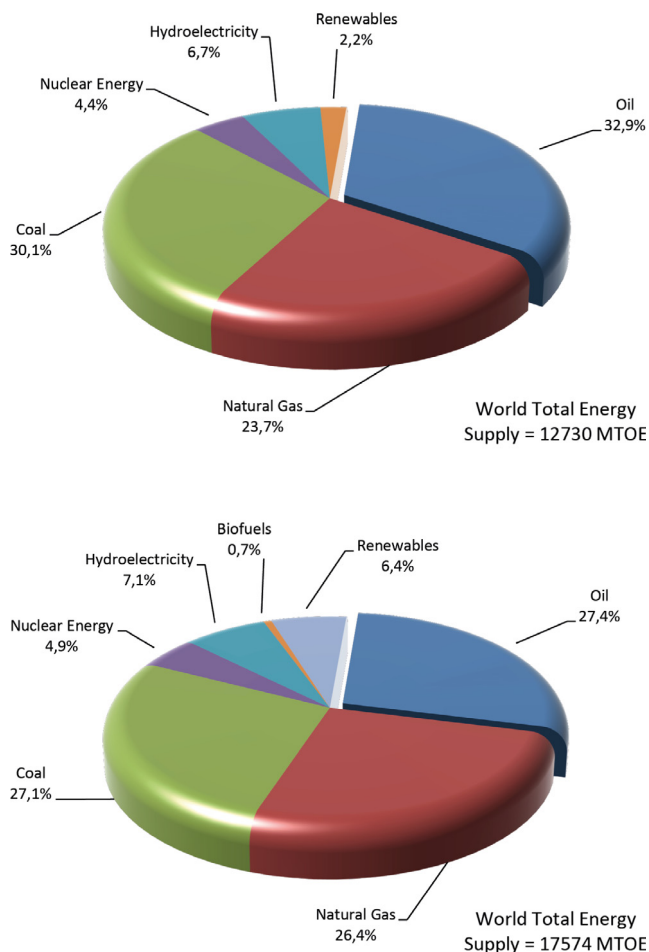

Fig. 2. World Energy Supply during 2014 (top) and forecast for 2035 (bottom) (adapted from BP [3,21]). MTOE stands for "Million Tons of Oil Equivalent", a unit of energy equivalent to 41.868 PJ.

2. Enhanced oil recovery

The main objective in all Enhanced Oil Recovery processes is to decrease the oil saturation below the Residual Oil Saturation (S_{or}) of a previous secondary recovery process. This is defined as the pore volume fraction occupied by the oil phase that remains in the rock formation after a displacement process has reached its economic limit [31]. It can be also defined as the saturation at which the oil production becomes discontinuous and is immobilized by capillary forces under ambient-groundwater flow conditions [32]. Enhanced Oil Recovery comprises a number of techniques based on the injection of fluids or other agents in order to modify determinate physical and/or chemical properties either in the fluids or in the reservoir, increasing the recovery factor and the lifetime of oilfields. These mechanisms can be categorized according to the following concepts:[24] increase the mobility of the displacement medium by increasing the viscosity of the water, decreasing the oil viscosity (or both simultaneously); increase the oil recovery at a microscopic scale by means of using viscoelastic fluids, which displace in a more effectively way the oil trapped in the porous media; extract the oil with a solvent; and reduce the interfacial tension (IFT) between oil and water and alteration of the reservoir rock wettability.

Enhanced Oil Recovery projects then are strongly influenced by economics and crude oil price. The cheapest oil currently comes from the conventional oilfield in primary or secondary stages. Fields already in EOR show an incremented cost and unconventional oilfields have the highest production costs to date (Fig. 6). The number of EOR processes skyrocketed in the mid-1970s and early 1980s due to the rise in the price of crude oil. Then, with the collapse of the latter during the mid-1980s, EOR projects plunged drastically simply because they became unprofitable, with the attention shifting to waterflooding and other IOR techniques. In recent years there has been a resurgence of EOR due to the increment in the oil price (Fig. 4) [22].

Enhanced Oil Recovery processes can be classified into three main branches, depending on the principles and physical properties on which the injected fluids act (Fig. 7).

The main objective of the chemical EOR processes is acting on one (or several) of the following factors: mobility (using viscosity-increasing water-polymer solutions), rock wettability and interfacial tension (IFT) (by adding surfactants and/or alkalis to the displacing agent). Thus, the factors influencing the oil recovery should be carefully analyzed before designing new chemical products for EOR. Furthermore, in order to improve the hydrocarbon recovery, it is important to have a clear understanding of the static and dynamic behavior of the whole system on various scales, from the field scale to the microscopic one (Fig. 8). In addition to the processes listed in Fig. 7, improved and more advanced methods have been developed combining several of them, such as: Polymer-Alternating-Gas (PAG), Alkaline-Polymeric Surfactant (APS) and Surfactant-Alternating-Gas (SAG). Furthermore, the use of nanotechnology in Chemical EOR has been lately reported, such as polymer nano-composites (PNP's or polymer coated nanoparticles) [33–39] and silica nanoparticles [39–50]. These developments have shown promising results both in laboratory and trial field tests. With respect to the nanotechnology, this cannot be considered as a new method in EOR, but as a boost of traditional techniques, which take advantage of the peculiar properties materials exhibit at the nanoscale. In EOR, the use of nanoparticles can be divided into: nanofluids which improve the recovery by means of enhanced rheological properties and the wettability alteration; nanoemulsions, more stable than those used in standard surfactant flooding; and nanocatalysts used in heavy-oil fields, acting as an "in-situ" refinery, upgrading the products in the rock formation itself [51]. A detailed description of other EOR techniques and nanotechnology is outside the scope of this review. The interested reader is kindly referred to existing literature on the topic [23,29,52–66].
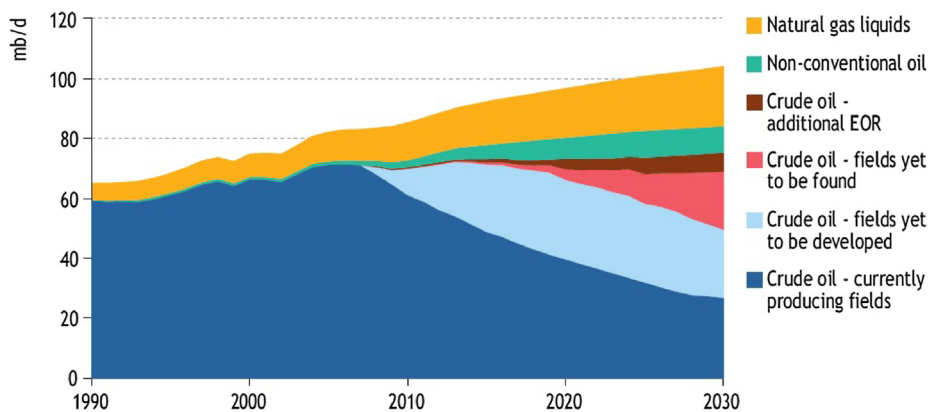
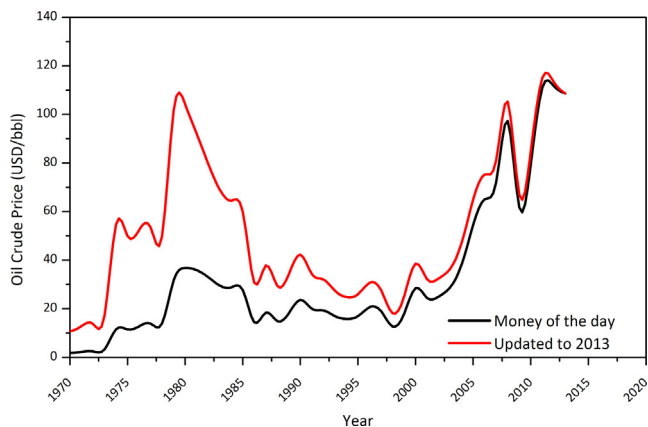**Fig. 3.** World Oil Production by Source in millions of barrels per day [22].

Fig. 4. Oil Price in dollars per barrel as a function of time (adapted from BP [3]).

3. Polymer flooding

One of the most effective chemical EOR processes consists in injecting a polymer solution to sweep the remaining oil from secondary processes to the production wells [68]. The first work proposing water-soluble polymers in EOR processes was reported by Sandiford [69], stating that the main functionality of the polymer was to increase the water viscosity used as displacing fluid [70]. The latter depends, among others, on the polymer concentration and molecular weight, temperature, water salinity, total dissolved solids (TDS) and the concentration of divalent ions. Furthermore, due to several developments reported by Wever [71–75], Lai [76,77], Kuang [78,79], Zou [80,81] and different authors [38,82–88], the polymer architecture is also an important factor to be taken into account. One example of this is the development of branched polymers (e.g., star and comb) which resulted in enhanced viscosifying properties with respect to traditional linear polymers. The branched structures give a higher number of entanglements, resulting in more viscoelastic solutions. This modification in the structure rendered improved recovery efficiencies in coreflood experiments compared to conventional EOR polymers.

Polymer flooding has the best application then in moderately heterogeneous reservoirs with low/medium viscosity crude oils (generally, less than 100 cP). Table 2 broadly outlines the general screening criteria applicable to this flooding technique. Nevertheless, Moe Soe Let [89] reports a successful polymer flooding in an oilfields in Suriname with an effective oil viscosity of around 400 ∼ 600 cP. In the United States, there has been a significant increase in the number of active polymer projects since 1978. These involve reservoirs having widely differing properties. This means permeabilities ranging from 20 to 2000 mD and reservoir temperatures of up to 93 °C. Water-soluble polymers for EOR applications also have been successfully implemented in Chinese oilfields, the most significant undergoing project is currently in the Daqing oilfield [90–92]. This arise was due to the result of government policies requiring oil companies to maximize recovery. Moreover, the rise in oil price has initiated a renewed interest of this
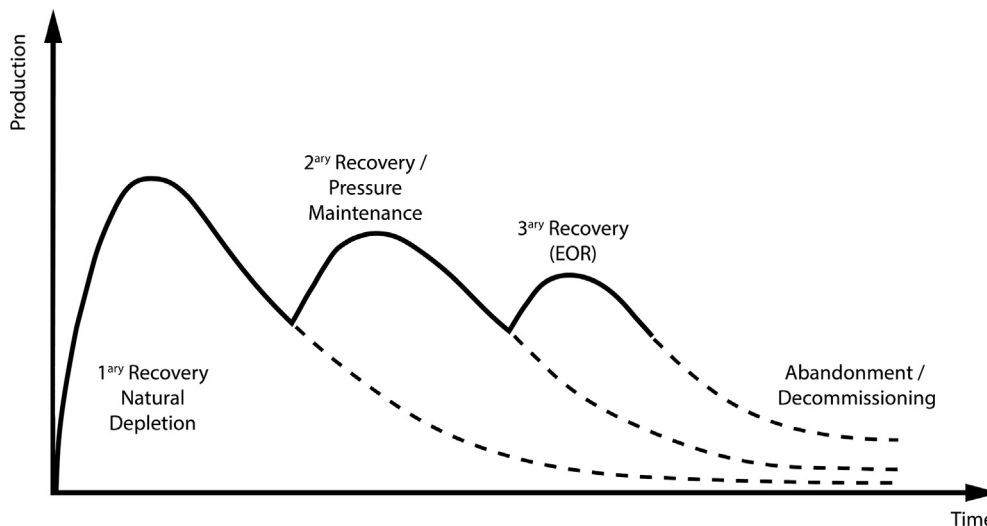

Fig. 5. Production scheme as function of time in an oilfield for the different recovery stages [29].
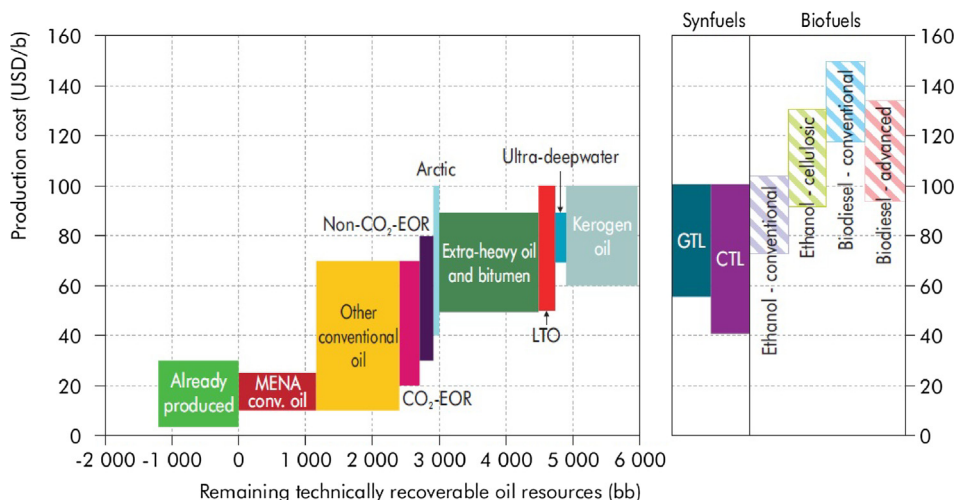
Fig. 6. Oil production costs in U$D per barrel for various resource categories [4].

technique among some international oil companies with projects underway in Angola, Oman as well as other regions including the UK North Sea [93–99]. For a detailed review the reader is referred to Dag Chun Standnes [100], who performed a comprehensive analysis of polymer field projects implemented in the field. With respect to polymer flooding in high-viscosity oilfields, it is important to point out the results presented by Delamaide [101,102]. The Pelican Lake field in Canada has a long history of operational problems due to two reasons: the high oil viscosity (up to 80,000 cP) and its thickness (<5 m). This makes it not suitable for thermal methods due to the heat loses and

moreover, waterflooding in this kind of system present a high mobility ratio, which increases the occurrence of water fingering. Then, in the mid 2000s, the combination of horizontal wells with polymer flooding rendered the best results, with recoveries of up to 25% of the OOIP and good water cut ratios.

In order to propose methods to improve this process, the mechanisms by which polymers increase the oil recovery should be firstly analyzed. For a long time it was considered that the polymer flooding only affected the macroscopic displacement [23,105–107]. This was achieved by lowering the mobility ratio and avoiding the unstable flow
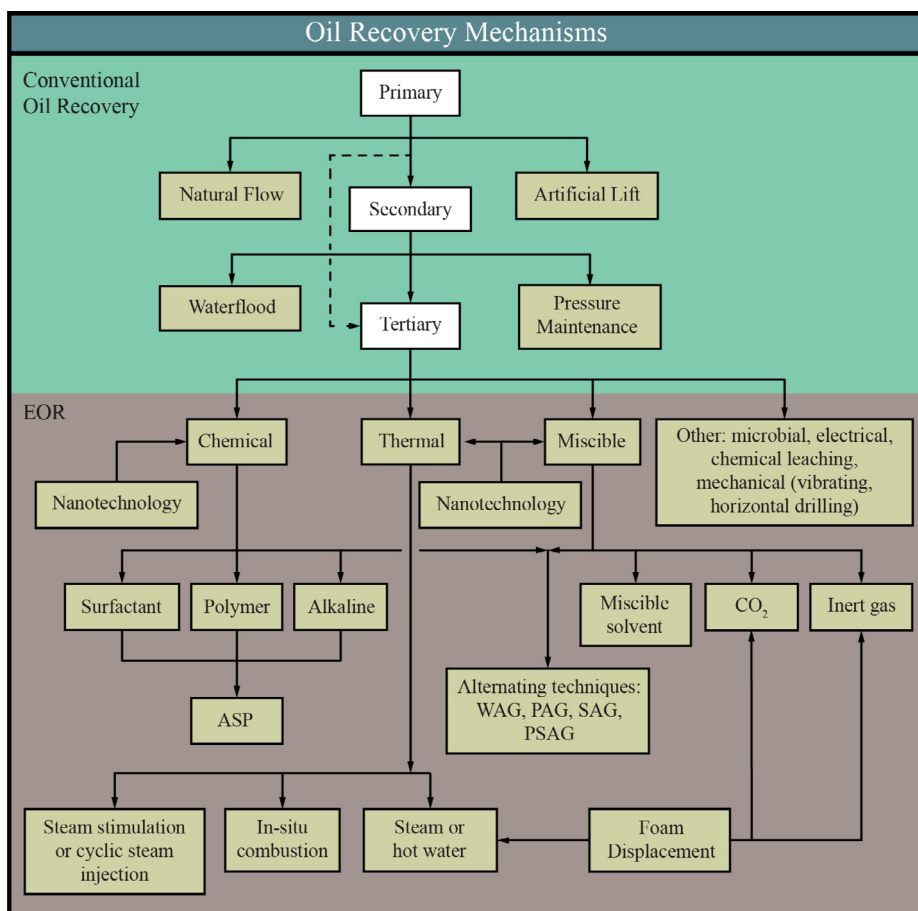

Fig. 7. Oil recovery stages and techniques (adapted from Schmidt [24]).
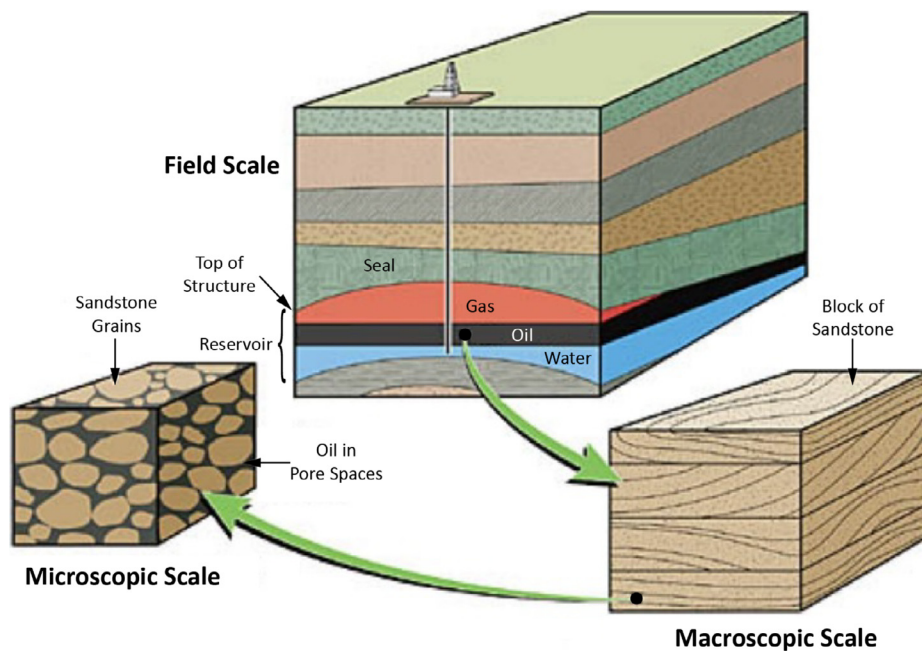
Fig. 8. Schematic view of the different scales involved in oil recovery processes [67].

Table 2
General screening criteria for polymer flooding processes [103,104].

Screening Parameter		Range/Value Recommended
Crude Oil		
Viscosity	cP	<150 (>1200 cP in low-thickness fields)
Gravity	°API	>15
Composition	–	Not critical
Reservoir		
Type of Formation	–	Sandstones preferred (carbonates also possible)
Depth	m	<2800 (due to thermal restrictions)
Temperature	°C	<95
Net Thickness	m	Not critical
Initial Reservoir Pressure	MPa	Not critical
Porosity	%	Not critical
Permeability	mD	>20 (preferred >50)
Initial Oil Saturation	% PV	>50
TDS	ppm	<20,000
Total Divalent Cations	ppm	<500
Special Remarks	–	Low Ca clay content

(viscous fingering), so the residual oil saturation S_{or} was not altered. The higher oil recovery was due to the capability of the polymer solution to contact and displace a higher amount of oil in the porous medium. However, in recent years experimental and field research suggest that the viscoelastic characteristics of the polymer solutions used indeed modify the displacement microscopic efficiency, reducing the residual oil, as the results presented by Wang [108–111], Zaitoun [112,113], Kamyabi [114,115], Wei [116,117], Wreath [118], Wang [119] and several authors [120–124]. Moreover, viscoelastic numerical models confirmed the different shear and mainly normal stresses created by fluids with viscoelastic behaviors when circulating in microscopic channels, such as those present in porous media [64,70,114,125–128]. Recently, De [129,130] presented the numerical modelling of multiphase viscoelastic fluids in porous media, using a FENE-P to model the polymer solution. However, to our best knowledge, very little is known on the numerical modelling of polymer viscoelastic solutions in porous media domains with multiphase fluids, stressing the importance not only of the elastic components but also of the interfacial behavior between the polymer solution and the oil phase. Therefore, we consider that coupled laboratory and numerical

experiments are advisable to predict polymer performance acting as displacing agent in porous media, in order to understand how the additional stresses generated by the elastic properties of the polymer molecules affect the sweeping process also at the interface level. In these, the physical domain should contain all the possible geometrical configurations present in the porous media, and not only the dead-end systems. Furthermore, these configurations should try to reproduce as accurately as possible the actual geometry and try to avoid pure theoretical models, which might lead to unrealistic results.

A different process also takes place, affecting the macroscopic displacement efficiency which is related to the fluids in the reservoir. While the oil relative permeability remains almost unaffected, the water relative permeability may be reduced. This is due to the following mechanisms:[116,117,131–133] segregation of flow pathways (water/oil); shrinking/swelling of polymer depending on phase flow; polymer absorption and entrapment in the porous media; and wettability alteration. This is known as Disproportionate Permeability Reduction (DPR) or Relative Permeability Modification (RPM) (Fig. 9), which is predominantly caused by polymer adsorption onto the rock formation [112,113,133–136]. Therefore, rock permeability is reduced when a polymer solution is flowing through it compared to the permeability when water is flowing. Because EOR polymers have relatively high average molecular weights (typically $>10^6$ Da) and extended chains, many polar groups along the polymer chain will attach to many different polar points on the rock surface [106,137].

Another factor to be taken into account is the inaccessible pore volume (IAPV). In the 70s, Dawson [138] noted that during flooding polymer molecules moved through the porous media more rapidly than salt ions in the solvent. They associated this to a fraction of the available pore space which was inaccessible to the large polymer chains, but accessible to the small solvent and salt molecules, and ions. Later on, Liauh [139] provided new possible mechanisms to explain the IAPV as the hydrodynamic exclusion of polymer molecules from low velocity regions adjacent to solid boundaries. He also related this phenomenon to the slow mass transfer of polymers in dead-end pores. Moreover, by examining molecular weight distributions of polyacrylamide effluent from cores, He [140] provided evidence that large molecules transit porous media faster than the small ones. The same effect was also observed in biopolymers by Lotsch [141] and Lund [142] as well as in associative polymers by Pancharoen [143].
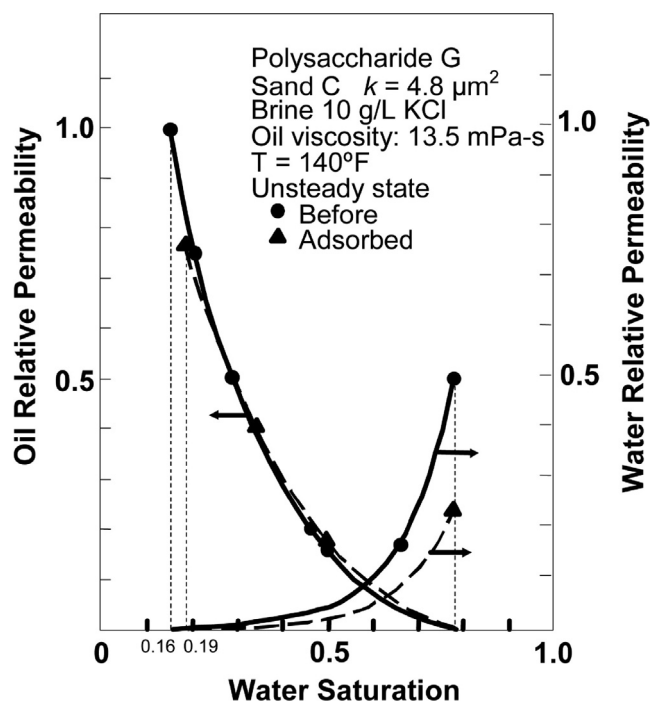
Fig. 9. Example of DPR in a sandpack showing the differences before and after the adsorption process took place [113].

Nevertheless, a special point of attention in polymer and in other EOR process is the possible consequences in the rock formation. This problem, known as formation damage, have been studied and evaluated for every type of agent used in tertiary recovery process, such as presented by Yuan [144]. In the case of polymer flooding, these problems are an excessive retention and particle plugging, decreasing the sweeping efficiency, and inorganic precipitation and organic deposition, caused by the interaction of charged groups in the polymer chain with salt present in the water. All in all, in order to establish criteria for synthesizing new polymers to be used in EOR, some requirements must be set. Taking into consideration the screening criteria set in Table 2, the following desired capabilities are listed, some of which are partially tackled by the new polymers and techniques described in this paper.

- Oil viscosity >150 cP.
- Low matrix-rock permeability (>1 mD).
- High reservoir temperatures (>95 °C).
- Hydrolysis resistant.
- Stability for long periods of time.
- Resistant to biological attack.
- Be environmentally friendly.
- Ability to withstand high level of TDS (>20,000 ppm), and total amount of divalent cations such as Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) above 500 ppm.

3.1. Polymers used

Products used as displacing agents can be divided into two major groups: synthetic and biopolymers. The most important polymers used in each group are presented and finally, the new developments made in the field are studied in order to understand how new chemical EOR agents can be developed from the existing ones.

3.1.1. Synthetic polymers

The base monomer of this class of polymers is the acrylamide (PAM, Fig. 10). However, this is not the only type of synthetic polymer used nowadays. PAM and its derivatives are presented during this section

and the recent developments such as Hydrophobically modified polyacrylamide, ethoxylated urethanes and alkali swellable emulsions will be analyzed in Section 3.4[73].

PAM was the first to be utilized as a displacing agent for chemical EOR, so it has been used as a reference system for subsequent modifications or improvements. The comparison can be either to check the increase in the oil recovery efficiency or to test their resistance to agents acting on detriment of their properties [73]. When used for EOR applications, polyacrylamides are used in partially hydrolyzed form (HPAM or PHPAM), therefore anionic carboxyl groups (COO^-) are distributed randomly along the backbone chain. These HPAM are the random co-polymers of acrylic acid and acrylamide (Fig. 11). Typical degrees of hydrolysis for EOR purposes are between 25 ~ 35%, resulting in the HPAM molecule to be negatively charged (polyelectrolyte). This degree of hydrolysis has been determined to optimize properties such as water solubility, viscosity and retention in the porous media. If the degree of hydrolysis is too small, the polymer viscosifying properties will not be relevant. If it is more than 35%, the solution properties will be too sensitive to salinity and hardness (TDS and Ca^{2+}/Mg^{2+}) [145].

The viscosifying property of HPAM lies in its high molecular weight (in EOR applications, the M_w is between $2 \sim 30 \times 10^6$ Dalton). This is further incremented by the anionic repulsion between polymer molecules and/or segments within the same molecule. This repulsion causes the molecules in solution to stretch and entangle with those similarly elongated, increasing the viscosity.

Nevertheless, a major problem arises when the brine salinity and/or hardness are higher than the levels mentioned in Table 2. The reason is that this repulsion is greatly decreased through ionic shielding of the electrolytes present in brine causing the polymer molecules to coil up. The shielding causes a corresponding decrease in the viscosity-effectiveness of the polymer since snagging is greatly reduced. This shielding increases as total dissolved salts increase, and at a constant TDS, it increases with the salt cations valency. Almost all HPAM properties show a large sensitivity to salinity and hardness [146], which becomes an obstacle for using HPAM in many reservoirs. The negative impact of divalent hardness ions, such as Ca^{2+} and Mg^{2+}, are much more significant, at the same concentration, than monovalent ions, such as Na^+ and K^+. This is one of the reasons why, when the TDS is analyzed, it should be known as well the proportion of these divalent cations present in the reservoir. A detailed description of how HPAM behaves under the presence of these cations can be found in the literature. Wever [73] and Peng and Wu [147] showed the dependence of the HPAM complexation as a function of the Ca^{2+} concentration and the degree of hydrolysis of the polymer. This leads to intrachain and/or interchain complexations (Fig. 12). The pH plays also a major role on the viscosity of HPAM solutions: decreasing the solution pH converts the anionic behavior of carboxylic groups to the non-ionic carboxylic acid form. The weakening the electrostatic repulsion along the polymer backbone leads to less viscosifying power for the polymer in a low pH solution [148].

As advantages, HPAM is relatively cheap and resistant to bacterial attack (significantly more than biopolymers) and it exhibits permanent permeability reduction. Also, the implementation of a HPAM flooding
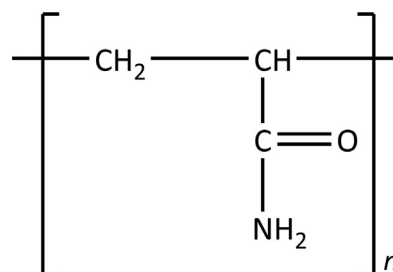

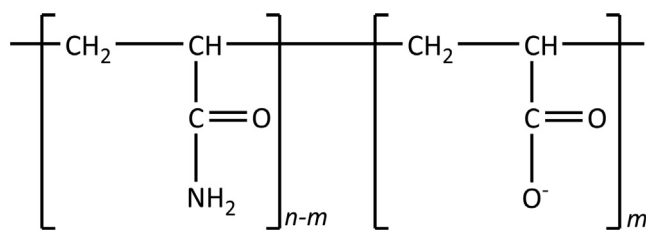**Fig. 10.** Chemical structure of the Polyacrylamide (PAM).

Fig. 11. Chemical structure of the Partially Hydrolyzed Polyacrylamide (HPAM) or poly(AA-ran-AM), where "*m*" denotes the grade of hydrolysis.

process is relatively easy and can improve significantly the oil recovery rate under standard reservoir conditions. This polymer can be used for temperatures up to 95 °C depending on brine and hardness. On the other hand, HPAM polymers are more susceptible to mechanical and shear degradation. Other disadvantages associated with HPAM are low thermal and shear stability, injectivity problems when high molecular weights and high concentration solutions are used for flooding. Some authors reported polyacrylamides degrade or precipitate in very high-temperature, high-salinity reservoirs [146,149,150].

The main goal in any tertiary EOR technique is to increase the oil recovery beyond the results obtained by secondary techniques, yielding a better use of the current non-renewable energy sources, extending as well the operational lifetime and economic profitability of mature oilfields. Since HPAM is widely considered to be the standard polymer EOR agent, it is usually used as the benchmark for improved EOR agents, and its performance is compared against traditional secondary recoveries(Fig. 13) [151]. Polymer flooding processes commonly take place before the economic limits are reached in waterflooding, allowing a reduction in the operation times as well as an increase in the production flowrates. This improvement in the recovery factor with standard synthetic polymer ranges from 10 up to 30% of the OOIP, depending on the oil viscosity, salinity, and temperature, among other factors. Regarding the economical aspect of the process, the total incremental costs of a polymer flooding can be divided in, namely: 1%
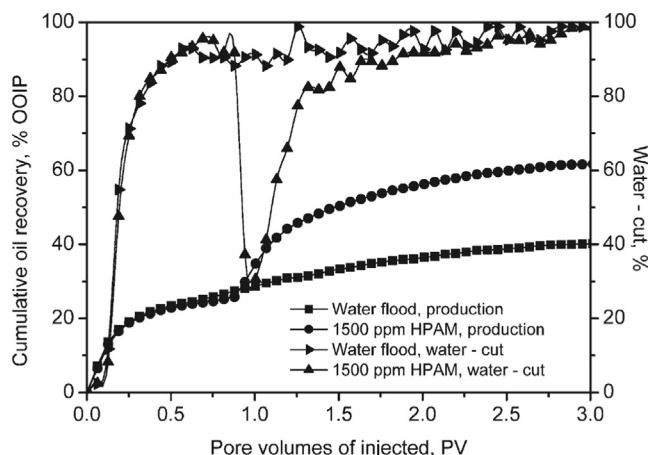
Fig. 13. Comparison of oil recoveries and water cuts in secondary and polymer flood tests [151].

from laboratory test and development of new products; 20–25% from the new facilities necessary to mix and inject the product; and finally 75–80% from the polymer itself. The cost of polymer alone represents an additional ranging between U$D 1 to 4 per incremental barrel of oil produced (e.g. in Daqing this value is 2.7 U$D/bbl), which renders a total cost between 20 and 35 U$D/barrel [152]. The additional production costs in typical polymer flooding can rise up to 15 U$D/bbl which is a function of the facilities necessary to set up the EOR process [73,153–155].

3.1.2. Biopolymers

Previously, HPAM was presented as the thickening agent in EOR processes. However, HPAM is categorized as not readily biological degradable and is a red chemical in some countries (i.e., OSPAR convention and the Norwegian Climate and Pollution Agency - KLIF). Therefore, the use (and potential discharge) of HPAM may be in conflict

Fig. 12. HPAM complexation in presence of Ca^{2+} cations [73,147].

with some countries' regulatory requirements. In order to meet these, new products must be designed so they can satisfy both the future environmental and energy requirements. Furthermore, the residual HPAM in the wastewater can slowly degrade into the toxic a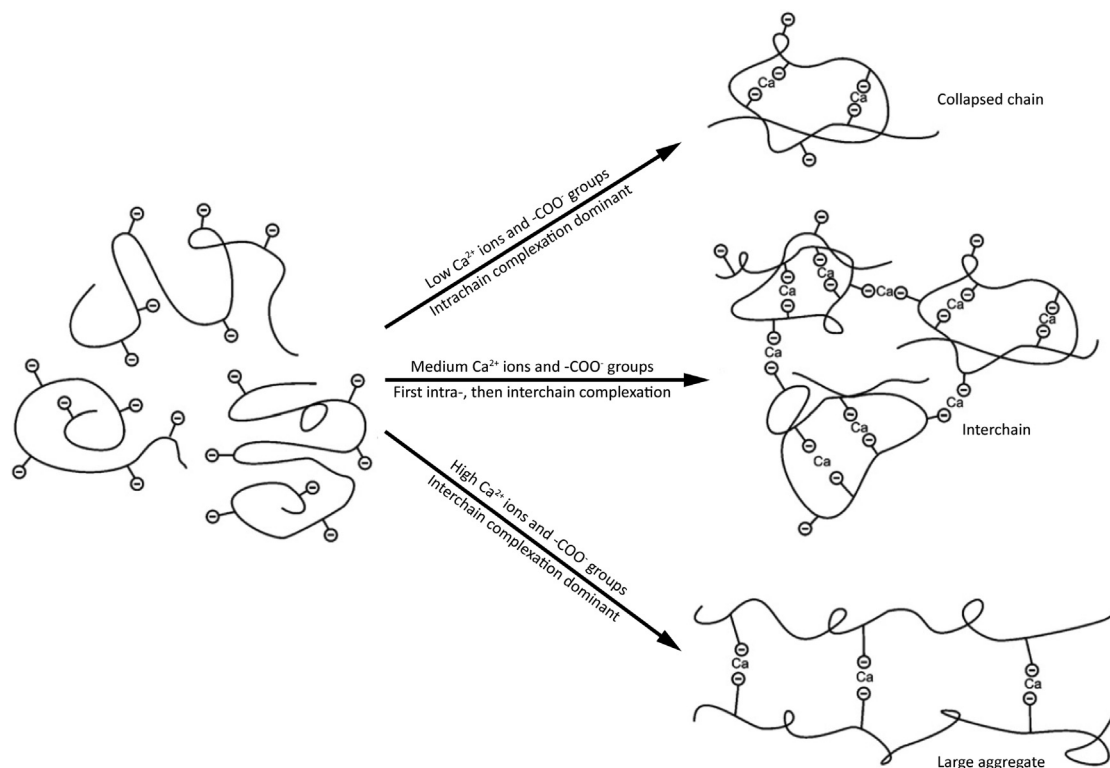crylamide monomer. Its toxicity has been studied by numerous researchers [156,157]. Since HPAM can remain in surface water and groundwater for a long period of time, it may endanger human health. This is the reason why some other more eco-friendly polymers are being used as viscosifying agents in EOR, such as polysaccharides biopolymers for EOR. Pu [158] reviewed these type of polymers, describing their main characteristics without making a comprehensive analysis of their chemical properties nor their application on the field. The polysaccharides used for EOR are: xanthan, scleroglucan, hydroxyethylcellulose, carboxymethycellulose, welan gum, guar gum, schizophyllan. From these, a study of the properties and chemical characteristics of the most important ones, Xanthan and Welan gum, is presented in this review [159].

Xanthan gum is a polysaccharide (Fig. 14) produced by the microbial action of Xanthomonas campestris on a substrate of carbohydrate media, with a protein supplement and an inorganic source of nitrogen. The biopolymer is an extracellular slime, which forms on the cells surface. Xanthan gum is well known to have excellent performance in high salinity brine [160,161]. It is relatively compatible with most surfactants and other injection fluid additives used in enhanced oil recovery formulations and the thickening property of this polymer comes from its high molecular weight (from 2 to 50×10^6 Da) [73].

One major problem with biopolymers is that these have often been consumed by anaerobic sulfate-reducing bacteria resident in oil reservoirs causing the generation of dissolved hydrogen sulfide (known as "souring") [162–165]. Because of this, it is usually injected along with an effective biocide to prevent microbial degradation. The effects of salt and hardness on the biopolymer properties and rheology are of relatively small consequence at lower temperatures (<80 °C), as compared with the effects on HPAM polymers that are used in similar conditions [105,166–169]. Han [90] reported the use of Xantham in field pilot projects the Daqing oil with satisfactory results under harsh salinity conditions (TDS 170,000). Xanthan gum is usually not mechanically shear degraded under polymer-flood injection conditions.

Another biopolymer which showed potential for its use in EOR processes is Welan gum [170–172]. It is produced by the fermentation of sugar by the bacteria of the genus Alcaligenes (Fig. 15). The polymer consists of repeating tetrasaccharide units with single branches of L-mannose or L-rhamnose. Its use in polymer flooding was due to the fact that exhibits viscosity retention at elevated temperature and stability in a wide pH range, also in the presence of Ca^{2+}. According to Xu [170,171], the rheological properties of welan gum are superior to those from xanthan gum solutions at various conditions, including superior viscoelastic properties.

It has been reported [73,170,171] that both xanthan and welan gum chains experience conformational transition from a disordered to an ordered, more rigid structure (Fig. 16). In Xanthan, this transition responds to changes in concentration, temperature and ionic strength [173–178]. The combination of high concentration and salts tend the solution to the ordered structure, and high temperature leads to the disordered ones. Something the similar occurs on welan gum, since it was reported that this biopolymer form under certain conditions double helices [170,171,179–182].

Regarding the performance in EOR processes, both Xanthan and Welan gum yielded similar recovery increases to those reported for HPAM, ranging from 10 to 25% of the OOIP (Figs. 17 and 18). Moreover, they showed a lower sensitivity to salinity and temperature than standard synthetic polymers (i.e. HPAM). In order to compare their efficiency, several flooding tests were performed in homogeneous sandpacks under the same operational conditions to assess as well their microscopic sweeping efficiency. The improvement obtained with Welan gum is associated to better viscoelastic properties related to its

conformal network structure, even at lower molecular weights than those from Xanthan gum (Fig. 16). Several pilot tests have been conducted with biopolymers showing an increase in the oil production with respect to traditional secondary processes and achieving a better stability than synthetic ones. However, their susceptibility to bacterial attack may increase the operational costs due to the necessity of additional products and facilities [170,183,184].

3.2. Polymer degradation

The average molecular weight of a polymer is an important parameter to be taken into account when a flooding is carried out. Any decrease on it, caused by chemical, biological, mechanical, or thermal degradation mechanisms, provokes a detriment in the properties of the solution and thus in the oil recovery.

3.2.1. Chemical

One of the causes of chemical degradation is the presence of free-radicals, which degrade both bio- and synthetic polymers. These radicals react easily and cause chemical chain-scission of the polymer. Examples of free-radical sources that can be problematic for flooding are: free oxygen (O_2), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO) and ammonium peroxide ((NH_4)$_2O_2$) [23,145,148,185,186].

Hydrolysis (autohydrolysis) reactions of the amide groups of the acrylamide polymers are one of the most important phenomena that take place in a reservoir. This causes a detriment in the viscosifying properties of the solution, especially in high temperature reservoirs containing a significant concentration of divalent cations in the formation water [187–191]. Sorbie [105] plotted the degree of polymer hydrolysis against time at various temperatures for 1,000 ppm PAM polymer dissolved in a brine of 5% salinity (Fig. 19). At temperatures over 80 °C (175 °F), his findings evidenced that the phenomenon takes preponderance, causing a major percentage of the PAM polymer to autohydrolyze, decreasing considerably its thickening properties. If an
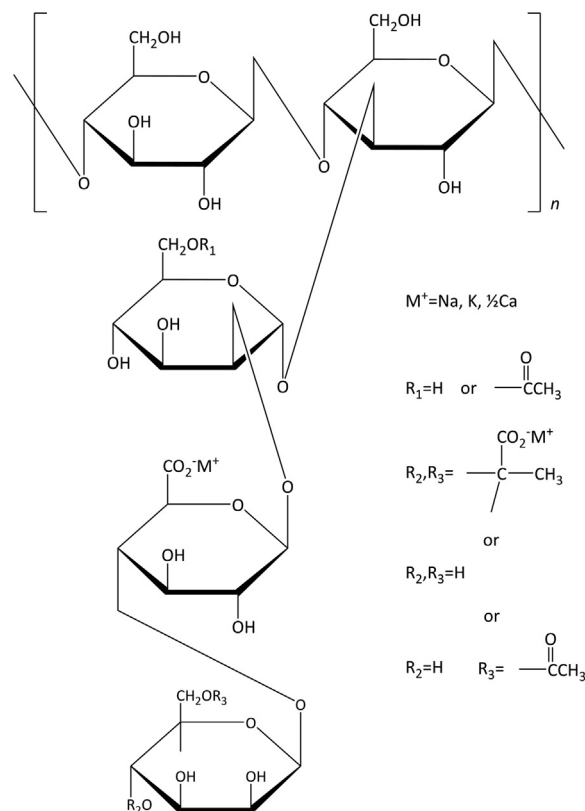

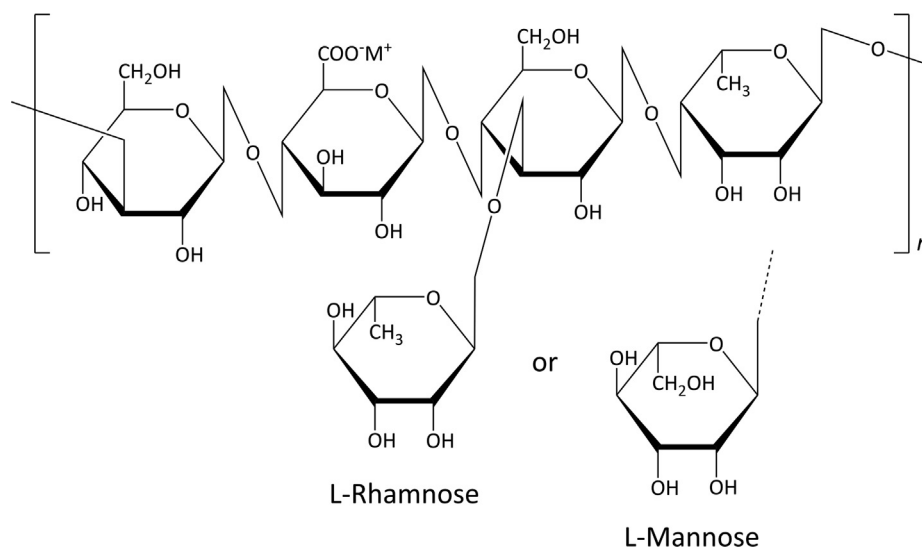**Fig. 14.** Chemical structure of the Xantham gum.

Fig. 15. Chemical structure of the Welan gum.

acrylamide polymer is used in such kind of environments, at high temperatures in water with high TDS, it will autohydrolyze experiencing a phase change, precipitating as undissolved solute. Thus, the polymer solution decreases its viscosity. Even though this type of autohydrolysis is not commonly considered polymer degradation, it leads to a phase change of the polymer, from being dissolved in solution to being an undissolved solid specie precipitating in the porous medium (Fig. 20).

3.2.2. Biological

Biological degradation is a serious potential issue for biopolymers [163–165], especially when used in shallow reservoirs and for those residing in surface tanks prior its injection. It is defined a chemical degradation of polymers when it is triggered by the action of microorganisms such as bacteria, fungi and algae. For a properly designed polyacrylamide flooding, potential biological degradation is essentially not a problem, whilst for biopolymers preventive measures must be

taken. However, different studies demonstrated also that biological degradation may also take place in synthetic polymers [70,157,193]. Sheng has reported that HPAM can provide nutrition to sulfate reducing bacteria (SRB). The consequence of this is a degradation of the HPAM molecules, thus decreasing the solution viscosity. Moreover, Bao [157] proposed a mechanism of HPAM biodegradation in aerobic medium (Fig. 21). After the biological attack, the backbone chain was cleaved and the HPAM was transformed into smaller uncharged molecules.

3.2.3. Mechanical

When polymers during a flooding process are subjected to high shear rates, a mechanical degradation occurs since these conditions cause chain-scission events [194–196]. This kind of degradation process is directly related with the polymer's molecular weight. During polymer flooding, high-flow shear rates might take place in surface-injection equipment (especially in Christmas trees, pumps and tubing), at downhole constrictions (tubing orifices, perforations or screens) and at
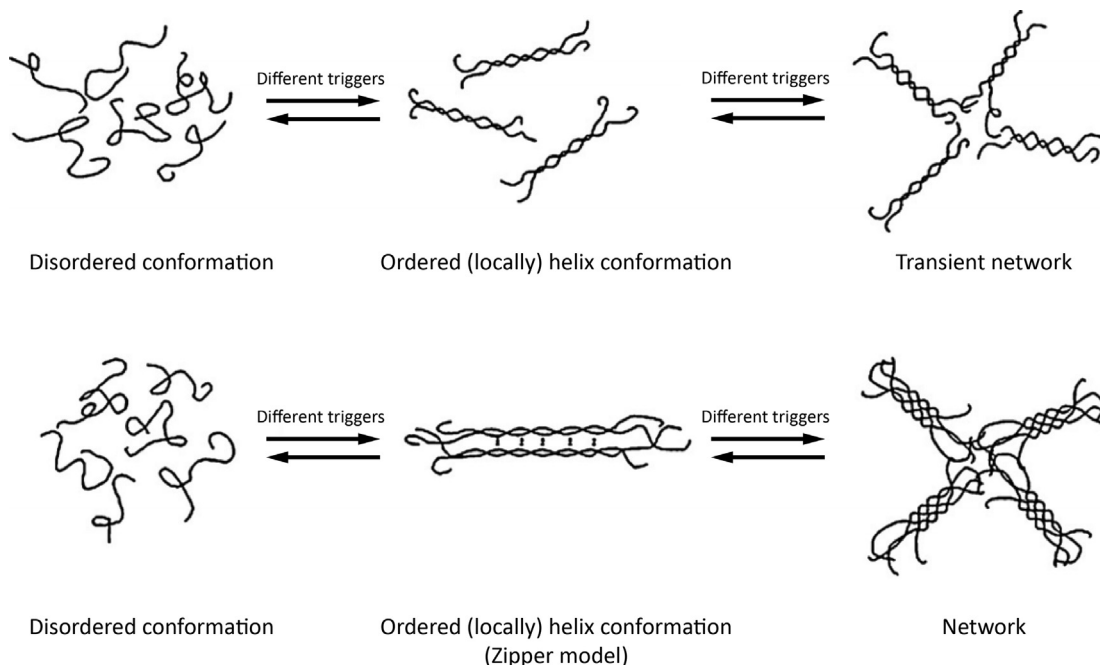

Fig. 16. Structural transition in Xanthan (top) and Welan gum (bottom) [73,170,171].
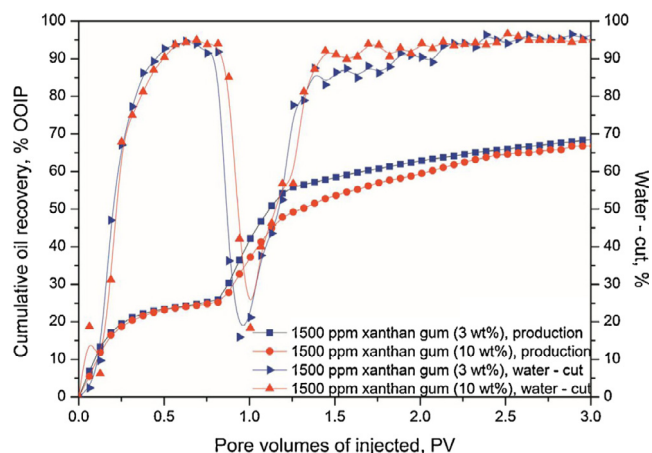
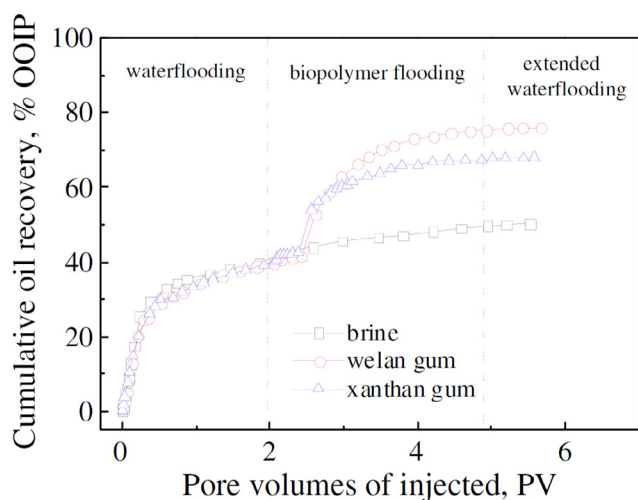**Fig. 17.** Comparison of oil recoveries in Xanthan gum polymer flood tests at different concentrations [183].

Fig. 18. Cumulative oil recovery in brine, Welan and Xanthan gum flooding tests, with a concentration of 1750 mgL^{-1}, temperature: 50 °C, salinity: 9374 mgL^{-1}, and a range of the permeability: 1.3–1.7 μm^2[170].
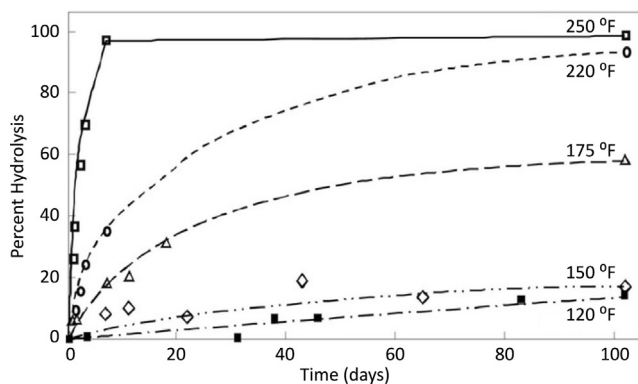

Fig. 19. PAM hydrolysis as a function of time and temperature [105].

the formation face. This is the reason why it is considered that the most significant part of the mechanical degradation occurs in the first moments after injection, before the chemical degradation takes place in the reservoir. Under most of injection conditions, high-M_w acrylamide polymers are quite susceptible to mechanical shear degradation [70,194,197–202]. This phenomenon is affected if the flooding brine is also high in TDS and divalent cations [203]. When a polymer solution is submitted to a high-shear rate flow, both shear and elongational

stresses diminish the polymer solution's viscosity [23]. Thus, even though increasing the molecular weight is one way to viscosify the solution [71], the bigger the chains are, the more susceptible and unstable the polymer is.

3.2.4. Thermal

All EOR polymer flooding processes have an upper temperature limit above which they are no longer chemically stable, and it is associated in HPAM polymers with the presence of salts dissolved in the brine (see chemical degradation). This temperature limit varies with water chemistries of both the polymer solution and reservoir brines, and the polymer chemistry. However, if only the temperature is taken into account without the presence of salts, polyacrylamide solutions show thermal stability under 200 °C, without a significant loss of mass [204,205].

3.3. Rheology of polymer solutions

Polymer solutions are well-known for exhibiting a non-Newtonian behavior, which means that its viscosity depends on shear rate. Furthermore, the length of polymeric molecules can be comparable to the pore throat length, which imparts certain elastic properties [206–209]. Polymer rheology in porous media affects both injectivity and sweep efficiency during an EOR flooding process, so it should be carefully analyzed in order to select the most appropriate polymers [210]. It is important to point out what happens with partially hydrolyzed polyacrylamide (HPAM) solutions. In porous media and in viscosimeters at high shear rates, HPAM solutions have been well-documented to show shear thickening after a critical shear rate (also called dilatant, pseudo-dilatant, and pseudo-viscoelastic behavior). Thus, the resistance factor increases with increased flux for moderate to high fluid velocities, which was observed and reported by Seright [211–215] and several authors who studied the rheological and viscoelastic behavior of polymer solutions in porous media and/or high shear rates [28,196,216–225]. At low velocities in porous media, a mild shear-thinning behavior has been reported [151,219,226–228], while different papers report also Newtonian or near-Newtonian behavior [212–215]. The critical shear rate depends on many factors like the degree of hydrolysis, concentration, temperature, the quality of the solvent and the polymer's molecular weight [73]. At even higher shear rates, the viscosity reaches a maximum and thereafter starts a second shear thinning region due to mechanical degradation of the polymer's molecules (see mechanical degradation) (Fig. 22).

The stability and viscosity of a polymer solution depends on multiple parameters, including: polymer concentration, salinity effects, intrinsic viscosity, presence of oxygen, reservoir temperature and shear rate. The polymer concentration has a direct relationship with the solution viscosity since an increase in its concentration results in an increment in the polymer viscosity. A correlation widely accepted is the empirical Mark-Houwink formula relating the molecular weight of the polymer (M_w) with the intrinsic viscosity [η][71].

$$[\eta] = K_{MH} \cdot M_w^{\alpha_{MH}} \tag{3.1}$$

where K_{MH} and α_{MH} are the Mark-Houwink parameters, which are characteristic for a given polymer-solvent pair at a specific temperature. The intrinsic viscosity is employed to calculate the solution viscosity at zero-shear rate, which is a parameter used in several rheological correlations (e.g., Carreau, UVM), and thus, based on the Mark-Houwink formula, a direct correlation may be inferred between the average molecular weight and the dynamic viscosity.

The rheological behavior of HPAM solutions below the critical shear rate can be modeled using the Carreau correlation (Fig. 23 and Eq. (3.2)). In a plot of viscosity against shear rate, HPAM displays a shear thinning behavior. This means that, as the shear rate increases, the fluid behavior will go from Newtonian (also called **Lower Newtonian** where the viscosity tends to be that at zero-shear rate), to shear thinning, and
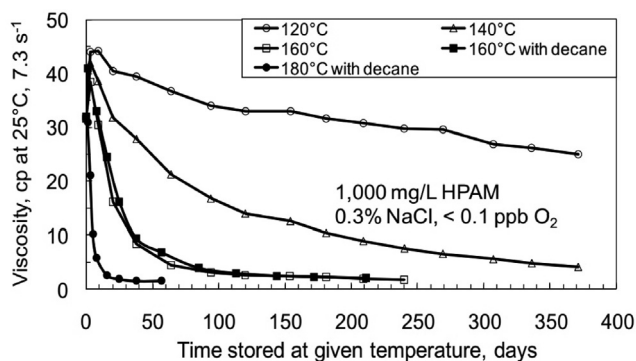
Fig. 20. Viscosity stability of a HPAM solution as a function of time at different temperatures [192].

then back to Newtonian (also known as **Upper Newtonian**). This apparent viscosity at zero-shear rate will remain constant for increasing shear rates until the shear thinning regime is reached [106]. In the last Newtonian region, the apparent viscosity asymptotically approaches the one of the solvent.

$$\mu = \mu_U + (\mu_L - \mu_U) \cdot \left[1 + \left(\frac{\dot{\gamma}}{\tau_r} \right)^2 \right]^{\left(\frac{n-1}{2}\right)} \tag{3.2}$$

where μ_L is the viscosity in the upper Newtonian regime, μ_U is the viscosity in the lower Newtonian region, and $\dot{\gamma}$ is the shear rate.

Moreover, a feature that HPAM solutions show is their negative thixotropic property (antithixotropy), this is a time dependence of the viscosity at a constant shear rate [73,229–235]. Bradna [236,237] has proposed, according to experiments, two different types of rheopectic behavior for HPAM solutions (Fig. 24), type I and type II. Rheopecty (or rheopexy) is the property exhibited by some non-Newtonian fluids which present a time-dependent increase in viscosity. The type I effect is observed at low shear rates with a slow but steady viscosity increase with shear-time up to an asymptotic value, what Bradna called "steady state viscosity" [238]. The type II effect was observed at higher shear rates and displayed as a sharp viscosity increase after a given shear-time, followed by a period of viscosity oscillation, then a sudden decrease and a subsequent slow increase [73,236,237,239,240].

3.3.1. Polymer rheology in porous media: shear thickening

The shear thickening behavior occurs in almost any highly turbulent flow in polymer solutions. This viscoelastic effect on the polymer appears beyond a critical shear rate which is characteristic for a given polymer type, molecular weight and solvent (Fig. 25). Shear thickening or the pseudo-viscoelastic response is a physical property that polyacrylamides exhibit when exposed to high velocities in a porous media [28,221,241–243]. In comparison to the rigid, rod-like molecular structure of biopolymers (which do not produce shear thickening behavior) [244], polyacrylamides are better described as flexible coils that adopt random configurations [106]. The flexible nature of the coil structure of polyacrylamide molecules is the cause of their ability to produce viscoelastic responses at high shear rates [28,106,226,245]. There are two primary reasons when considering this behavior of shear thickening. The first is a characteristic of the porous media, and it is the time it takes for a polymer molecule to travel from one pore throat to another which is effectively dependent on the space between pore throats [28,106]. The second characteristic, which affects the presence of viscoelastic behavior and is related to the polymer solution, is time required for the polymer molecules to go from an elongated form back to a relaxed coil configuration [226]. This is referred to as the relaxation time (t_{rel}) and it is usually measured in the laboratory.

In order for shear thickening to occur, the polymer relaxation time must be of the same order of magnitude, or larger, than the time it takes for the polymer to travel between one constriction to another. The Deborah Number is a dimensionless relationship between the time scale of observation (t_{obs}) and the polymer solution relaxation time. This group is useful in correlating the properties of the fluid-rock system with the onset of viscoelastic or shear thickening effects [28,226,245].

$$De = \frac{t_{rel}}{t_{obs}} \tag{3.3}$$

3.3.2. Viscoelastic models

Thus far, in the rheological models described before, the shear-dependent fluids were assumed to be non-elastic. However, some polymer solutions show elasticity to variable extents. When an elastic substance is deformed through a small displacement, it tends to return to its original configuration. Viscoelastic flow exhibited by polymers in porous media is different from the flow of Newtonian fluids, in which the viscosity contribution to the normal stresses is generally considered negligible due to the fluid incompressibility [246]. However, in viscoelastic fluids a general state of stresses (normal and shear) is fully developed. Due to the continuous stretching and recoiling of polymeric molecules as they flow through porous media, they develop an additional "elastic viscosity" which improves the microscopic sweep efficiency. Through micro-seepage polymer flooding experiments, Guo [247] concluded that additional oil recovery was observed due to greater shear stress between polymer-oil than between water-oil. Due to
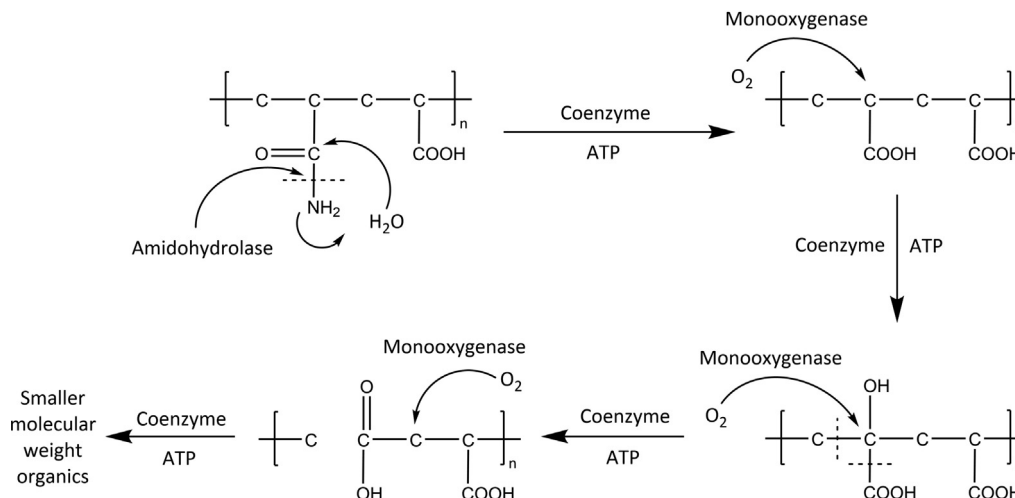

Fig. 21. Hypothetical mechanism of HPAM biodegradation in aerobic condition (Adapted from Bao [157]).
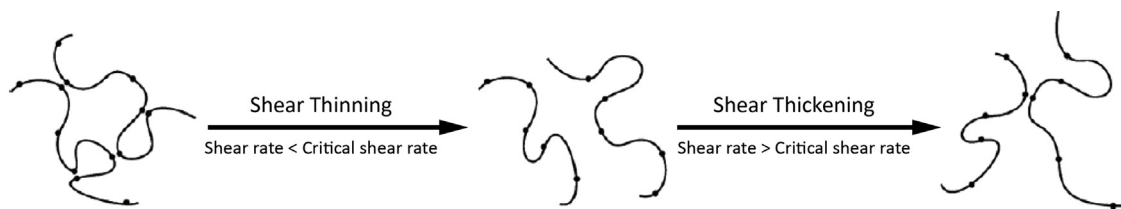
Fig. 22. Behavior of HPAM coils at different shear rate conditions [73].

these viscoelastic properties, a normal stress will appear between oil and polymer, hence the displacing agent exerts a pulling force over residual oil trapped in the porous media. Oil is "pushed and pulled" out of dead-end pores [108–111]. In order to improve the microscopic displacement efficiency and to model numerically what are the mechanisms involved in the process, it should be clearly established beforehand how the oil is trapped at a microscopic scale. The residual oil trapped can be classified in four different physical configurations: residual oil in dead ends; oil ganglia in throats trapped by capillarity forces; oil film on pore walls; and oil unswept in heterogeneous parts of the porous media (Fig. 26) [71,126,127].

Zhang [127,126] used constricted/expanded channels to model the pore throats in porous media and numerically studied the flow of viscoelastic polymer solution in a pore throat model. It was found that a smaller throat size leads to greater "elastic viscosity" and higher flow resistance. The micro-swept coefficient rises with the increase of the elastic properties of the polymer solution. Viscoelastic polymers can penetrate deep into the rock pores and efficiently displace oil, improving the overall oil recovery and reducing residual oil saturation. Zhang [128] considered, in order to model the viscoelasticity effect, that the apparent viscosity of the polymer solution was in fact a sum of two components. The first one, purely viscous which had shear-thinning behavior at high shear rates, and an "elastic viscosity" which becomes predominant also at these shear rates, increasing the apparent viscosity of the fluid, creating a shear-thickening fluid. This same approach was utilized by Delshad [227] on the unified viscosity model (UVM). This model consists of two parts: a shear thinning (μ_{SH}) and an elongational-viscosity dominant regions (μ_{ELAS}). The shear thinning is calculated using the Carreau correlation, explained previously. The UVM then can be expressed according to Eqs. (3.4) and (3.5), where μ_{MAX}, λ_2, τ_2 and n_2

depend on the solvent viscosity and the polymer concentration.

$$\mu_{UVM} = \mu_{SH} + \mu_{ELAS} \tag{3.4}$$

$$\mu_{ELAS} = \mu_{MAX} \cdot [1 - e^{-(\lambda_2 \tau_2 \dot{\gamma})^{n_2-1}}] \tag{3.5}$$

These mechanisms were also modeled numerically applying mathematical viscoelastic models used for disperse polymer solutions (such as Upper Convected Maxwell, Oldroyd-B and FENE). They confirmed the theory that polymers do affect microscopic efficiency, hence they are able to modify the residual oil saturation in the reservoir [108–111,126–128,208,209]. Nevertheless, these models were mostly not based on two phase displacement but just in terms of flow velocity, stress components and pressure fields. In this context, the use of numerical simulators in order to make an accurate representation of a polymer solution flooding would be useful, since a single phase flow does not take into account the important interactions taking place at the interface between two fluids in a displacing process.

All things considered, compared with the non-elastic solutions, the required injection pressure of viscoelastic polymer flooding will be higher. This causes that the injection of the EOR agent becomes more difficult as long as the elastic properties of the polymer solution take relevance. This is still a challenging issue in polymer flooding techniques [111].

3.4. New products and techniques for polymer EOR

Several modifications have been suggested to make polyacrylamides resistant to the temperatures generally found in oilfields. One of these alternatives is AM-co-AMPS, a copolymer that can be used up to 90 °C in high salinity reservoirs, with better thermal stability and performance
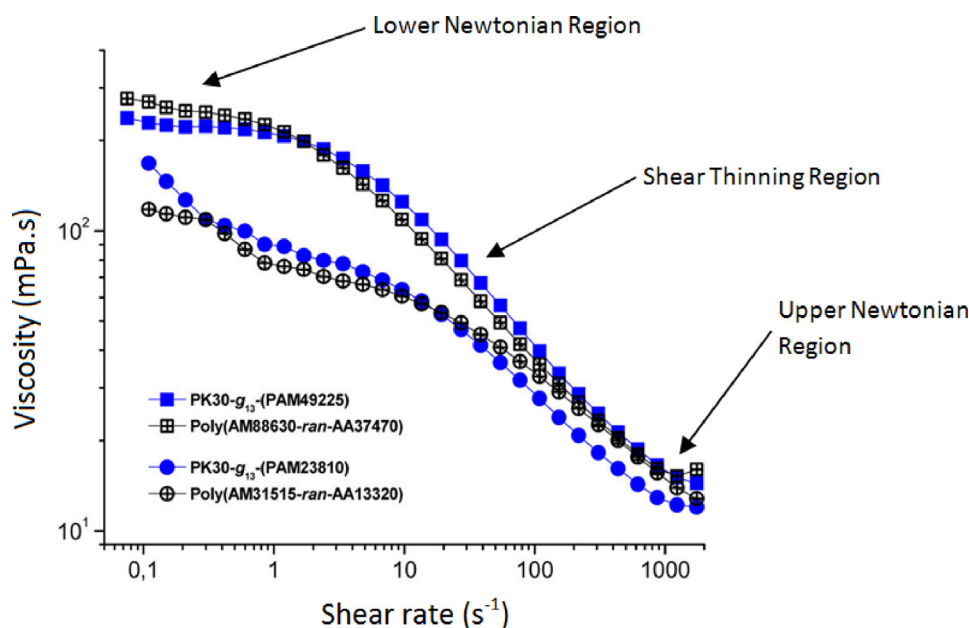

Fig. 23. Example of the Carreau viscosity model. The graph shows the solution viscosity as a function of the shear rate of four branched polymers ([p] = 5000 ppm) [71].
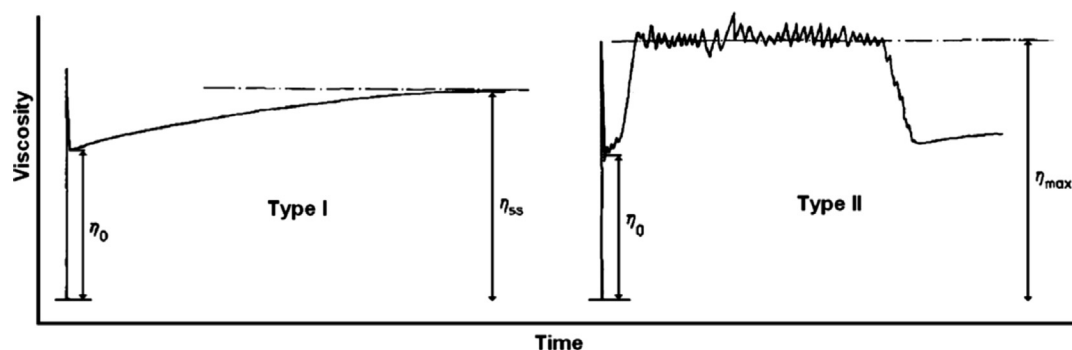
Fig. 24. Rheopectic behavior of HPAM solutions [236].

than HPAM [70,248–251]. Sabhapondit [252] also reported the development of a new copolymer made of N,N-dimethyl acrylamide with Na-2-acrylamido-2-methylpropanesulfonate (NNDAM-NaAMPS) which performed well on tests and moreover it was found to be thermally stable at 120 °C at least for a period of 1 month (Fig. 27). It was further confirmed by experiments that the residual oil recovery increased with the increase of temperature. Also, Stahl [189,190] presented the synthesis of a copolymer of vinylpyrrolidone (N-Ethenyl-2-pyrrolidone) and acrylamide (NVP-co-AM), reporting that a sample remained in synthetic seawater at 121 °C for over six years without precipitation. Gaillard [253,254] synthesized polymers based on acrylamide (AM), sodium acrylate (AA-Na), sodium acrylamide-tertiary-butyl sulfonate (ATBS) and N-vinyl pyrrolidone (NVP), testing their thermal stability at temperatures up to 120 °C and TDS up to 70,000 ppm with high hardness content, finding that both NVP and ATBS improved thermal and salt stability, withstanding these conditions with minor loss of viscosity during at least 1 year. A disadvantage regarding these copolymers of NVP is its higher cost as compared with HPAM polymers [255].

The extreme sensitivity to certain parameters present in reservoirs by the HPAM polymers (and its derivatives) has triggered out during the last years extensive research and development in the subject. A key factor in a successful polymer flooding is the rheological properties of the aqueous solution. Three different lines of investigation can be distinguished about the improvement of the efficiency in polymer flooding: the development of hydrophobically modified polymers, which take advantage of intra and intermolecular associations of hydrophobic groups in order to enhance the thickening capabilities; the development of hyper-/branched polymers, which takes advantage on a change in the (macro)molecules' architecture, increasing the

entanglement and thus the solution viscosity; and the use of colloidal dispersion gels (CDG's), which behave in a comparable manner as hydrophobically modified polymers but using crosslinkers as the element to form the association among molecules.

The hydrophobically modified polymers are synthesized by introducing a number of hydrophobic groups to the polymer's hydrophilic backbone chain, achieving higher thickening capabilities [256]. These groups can be located along the backbone chain randomly or in blocks, and coupled at one or both ends (Fig. 28). In aqueous solutions at a basic pH, hydrophobic groups form intramolecular and intermolecular associations that create a three-dimensional network [257], hence significantly increasing the solution viscosity. Another important fact is that these polymers are less sensitive to brine salinity compared to a conventional HPAM solutions [257]. Associative water-soluble polymers were tested and showed promising results compared to traditionally used polymers. Several studies demonstrated that, besides the fact that oil is produced faster (compared to water flooding), the recovery factor efficiency is also increased [73,258]. Among these group of associating polymers, the next developments may be named: Hydrophobically Modified Polyacrylamide (HMPAM) or Hydrophobically Modified Associating Polyacrylamide (HAPAM); Ethoxylated Urethane (HEUR); Hydroxyethylcellulose (HMHEC); Alkali-swellable emulsion (HASE); Partially Hydrolyzed Microblock Hydrophobically Associating Polyacrylamide (HMBHAP) and Branched Hydrophobically Modified Polyacrylamide (BHMPAM).

Hydrophobically modified alkalisoluble emulsion (HASE) polymer is one class of water-soluble associative polymers that contains a small number of hydrophobic groups [260–262]. The hydrophobically modified polymers have either a telechelic structure in which the chains are end-capped with the hydrophobic groups, or more complicated comb-
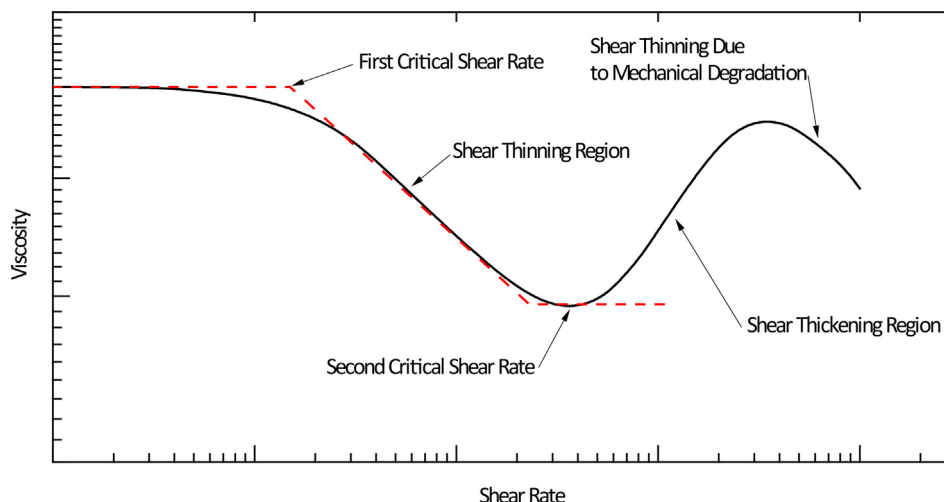

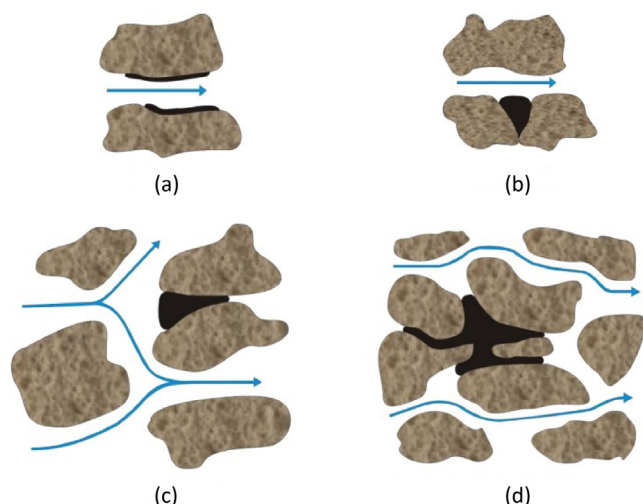Fig. 25. Rheology behavior of polymer solutions in porous media.

Fig. 26. Oil residual schemes at poral scale: oil film adhered to pore walls (a), oil trapped in dead ends (b), oil trapped due to heterogeneous porous media (c) and oil ganglia in pore throats (d) [71,127,126].

like structures in which these groups are randomly grafted to the polymer backbone [263]. The backbone has a polyelectrolyte feature and is composed of a polymer of acrylamide or acrylic acid and ethyl-acrylate [260,264]. For a deeper study of the chemistry involved in these developments, the reader is kindly referred to the appropriate literature [73,78,79,82,265–276].

The application of hydrophobically modified polymers has showed also a great potential for EOR applications, especially in oilfields with harsh conditions where conventional HPAM-based polymers lose efficiency due to the increased salinity and temperature. It is reported that in average these kind of polymers can increase the oil recovery up to a 15% with respect to traditional ones (Fig. 29). The inter- and intramolecular associations improve the viscoelastic properties of the solution, which renders better microscopic sweeping efficiencies. A disadvantage with respect to traditional polymers is the higher production costs, which may limit the applicability of these polymers when the economic conditions (i.e. oil barrel price) are not met. It is expected that in future years, which higher oil prices, the profitability with these

polymers will improve and their application will become a standard procedure [277–279].

Another recent development in this field was to introduce a new concept to increase the viscosity of the solution, and it was by synthesizing hyper-/branched PAM. Instead of using M_w or concentration in order to viscosify the solution, the change in the architecture of these polymers proved to be an efficient way to face the problems previously mentioned (e.g., branched, star or comb type polymers). These new branched macromolecules are formed by a central structure around which a certain number of arms are developed (Fig. 30) [71].

These polymers showed superior strength than traditional ones against salts, as well as an increased oil recovery in laboratory studies [72,74,75]. However, few research had been done on the numerical modeling and simulation of these products and its rheological behavior in flow cells or cores. Also, it is important to understand the relationship between the number of arms, their molecular weight and structure with the rheological properties and the degradation processes in order to assess their efficiency in future EOR applications.

The hyperbranched polymers evidenced improved performances with respect to traditional linear ones in flooding processes. This is due to the fact that the polymer architecture allowed a higher number of molecules entanglements, which translates into better viscoelastic and rheological properties. Thus, the microscopic efficiency is improved and the lower residual saturations can be achieved (Fig. 31). Several authors have reported increases of up to 20% beyond traditional linear-polymer flooding processes, with higher recovery values of up to 35% in coreflooding tests [71,77,280]. However, certain topics must be addressed before a field application is carried out: the pressure in the injection wellhead is also higher due to the solution viscosity, and therefore the facilities must be verified and adapted in order to withstand the higher stresses. Furthermore, the syntheses techniques for this type of polymers must also be investigated in order to scale it up to industrial levels, from the Atomic Transfer Radical Polymerization (ATRP) process used by Wever [71] to the Reversible Addition-Fragmentation chain-Transfer Polymerization (RAFT) presented by van Mastrigt [281].

The enhanced viscoelastic properties allow hyperbranched polymers to penetrate deeper in the pore throats and dead-ends, and pull the oil out, lowering the residual oil saturation with respect to traditional agents (Fig. 32). The extra normal stresses generated by the elastic
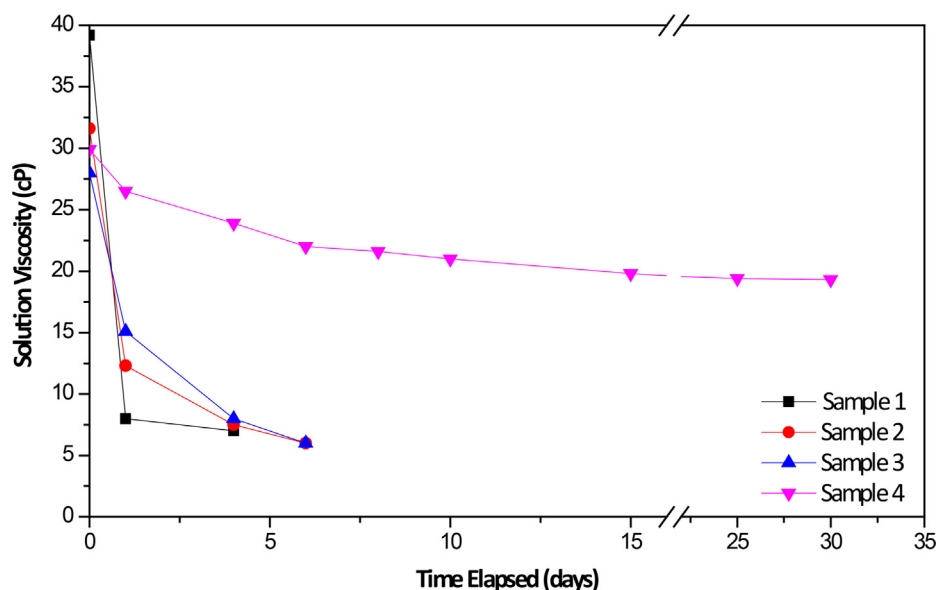

Fig. 27. Solution viscosity ($\dot{\gamma} = 1312\,\text{s}^{-1}$) at 25 °C (concentration 0.8% aqueous solution) after aging at 120 °C for four different copolymers [252] The samples correspond to the following copolymers: Sample 1–70% AM and 30% AA; sample 2–70% AM and 30% AMPS; sample 3–70% NNDAM and 30% AA and sample 4–70% NNDA.M and 30% AMPS.
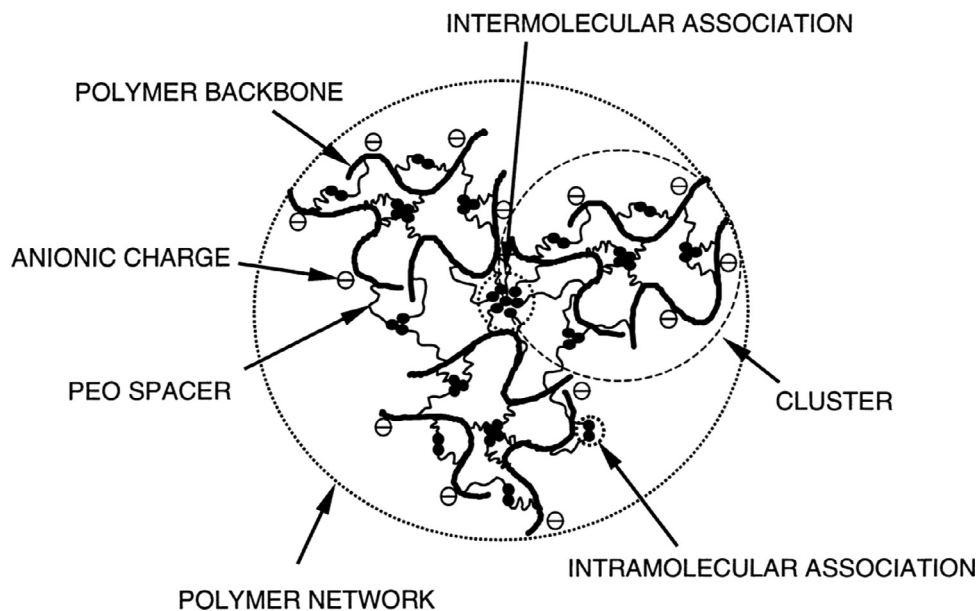
Fig. 28. 3-D network structure of associative polymer in aqueous solution [259] The polymer is composed by methacrylic acid (MAA), ethyl acrylate (EA), and a macromonomer capped with a hydrophobic group through poly-(ethylene oxide) (PEO) chains.
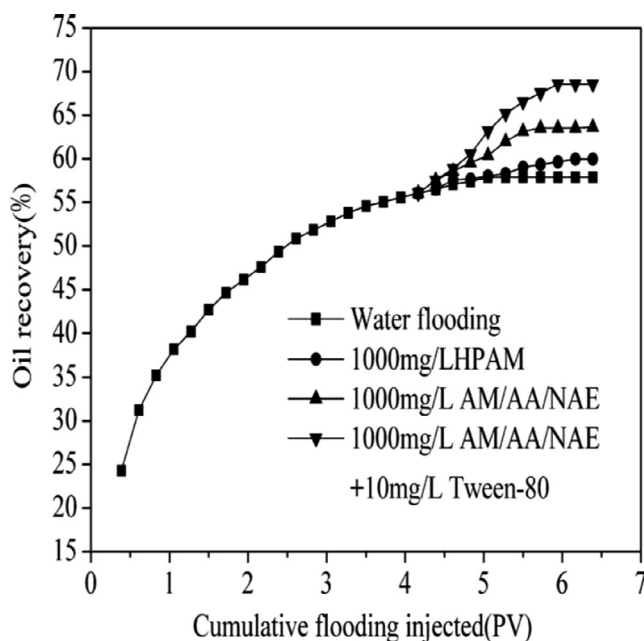

Fig. 29. Results of coreflood tests of a secondary flooding, HPAM and a hydrophobically modified polymer in laboratory experiments [277].

forces of the polymer molecules allow obtaining better oil recoveries than traditional non-elastic viscous fluids, such as waterflooding processes. Moreover, linear polymers do not reach the same level of entanglement in the solution as hyperbranched, rendering lower oil recovery saturations [74,282].

Finally, a technique that has been in development during the last years is the use of Colloidal Dispersion Gels (CDG's) or Linked Polymer Solutions (LPS's) as displacing agents for mature reservoirs. Basically this process is an enhanced polymer flooding, consisting in the injection of a traditional high M_w polymer, like HPAM, at lower concentrations than standard polymer flooding processes (typically ranging from 100 ppm to 1000 ppm), and a crosslinker (generally Aluminum Citrate or Chromium acetate) in a polymer/crosslinker ratio ranging from 10 to 100. The main function of the crosslinker is to form intra and inter

molecular associations, in a similar way as it happens with hydrophobically modified polymers. These associations depend, among other factors, on the polymer type and concentration, polymer/crosslinker ratio and crosslinking temperature. In dilute solutions, below the critical overlap concentration (c∗), intramolecular associations are predominant. This causes the polymer molecules to coil up independently, creating dispersed particles of finite size. In semi-dilute solutions, with concentrations above c∗, there will be a combination of intra and intermolecular bonds. At even higher concentrations (concentrated solutions), intermolecular associations will be predominant. Together they generate a gel in-situ, improving the mobility and recovery factor. The advantage of this method is that achieves higher viscosities using low polymer concentration. It is also considered that one of the main mechanisms to improve oil recovery is the "log-jamming" effect or pore blocking, diverting the water flow and thus improving the microscopic efficiency (microscopic water diversion). In the presence of this multivalent cation (the crosslinker which consists of spherical nanoparticles around 50–150 nm) multiple anionic groups of the HPAM (carboxylic groups) bond to the former creating intramolecular and intermolecular crosslinkings [95,283]. The enhanced properties of CDG's over standard polymer flooding processes are found useful in heterogeneous formations (Dykstra-Parsons coefficient >0.5). This is due to the fact that in non-uniform rock permeabilities low volumetric sweep efficiencies are achieved and under such conditions, uncrosslinked polymers are not capable to overcome these heterogeneities. This technology was first mentioned during the 70s and 80s when Phillips Petroleum investigated a process combining sequential injection of PAM with Aluminum Citrate in the North Burbank Field [284,285], reporting an increase in the recovery factor.

Subsequently, the process was modified during the 90s and instead of injecting alternated slugs, both polymer and crosslinker were mixed prior injection rendering good results [286–288]. There has been studies of successfully CDG's flooding in China's giant Daqing field [289]. Smith [288,290], carrying out laboratory experiments, corroborated the CDG's behavior in core floods, finding them consistent with the reported field results in Daqing. Lobo [291] summarized the process from the laboratory to the field evaluation in Dina Cretaceous Field in Colombia. The laboratory studies include basic fluid/fluid evaluation, CDG formulations and coreflood tests, beginning the CDG field application in 2011. CDG injection strategy considered a fixed polymer
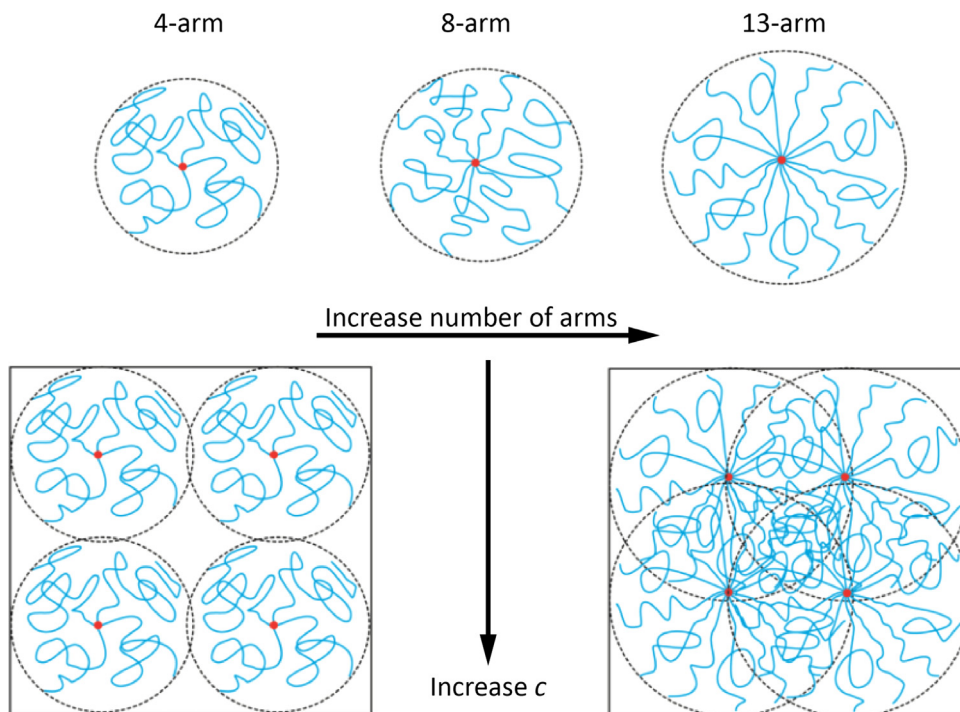
Fig. 30. Several configurations for branched HPAM (adapted from Wever [71]).
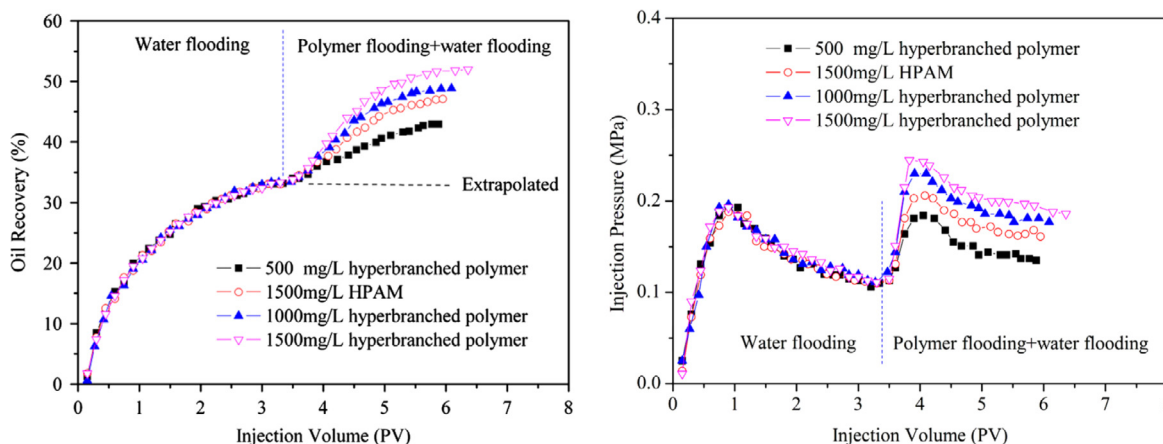
Fig. 31. EOR capabilities of branched polymers (left) and injection pressures during the flooding processes (MPa) (right) [76].

concentration of 400 ppm and a polymer/crosslinker ratio ranging from 40:1 to 80:1. The operational results showed an increase in oil recoveries and reduction of water cut. Moreover, in the Loma Alta Sur field (Argentina), chromium (III) was the multivalent cation applied [292], yielding a positive change of trend in oil production. Manrique [293] made a comprehensive review of 31 CDG's ongoing projects in Argentina, Colombia and the U.S. providing results that CDG's can be

injected into the reservoir without injectivity constraints. Finally, several experiments were presented in order to study the behavior and performance of difference polymers and crosslinkers in porous media, showing positive results and a potential in operational fields [294–300].

As example of the performance of CDG's in EOR applications, the Dina Cretaceous field in Colombia was used in a field test to assess the
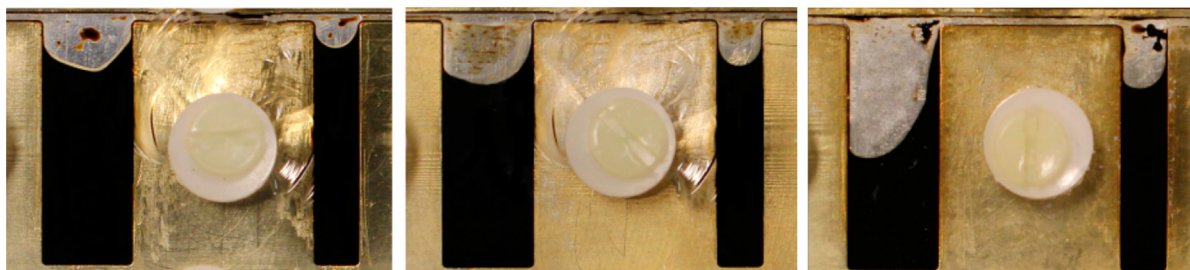
Fig. 32. Flowcell displacement processes from dead-ends carried out with brine (left), linear HPAM (middle), and a branched polymer (right) [74].
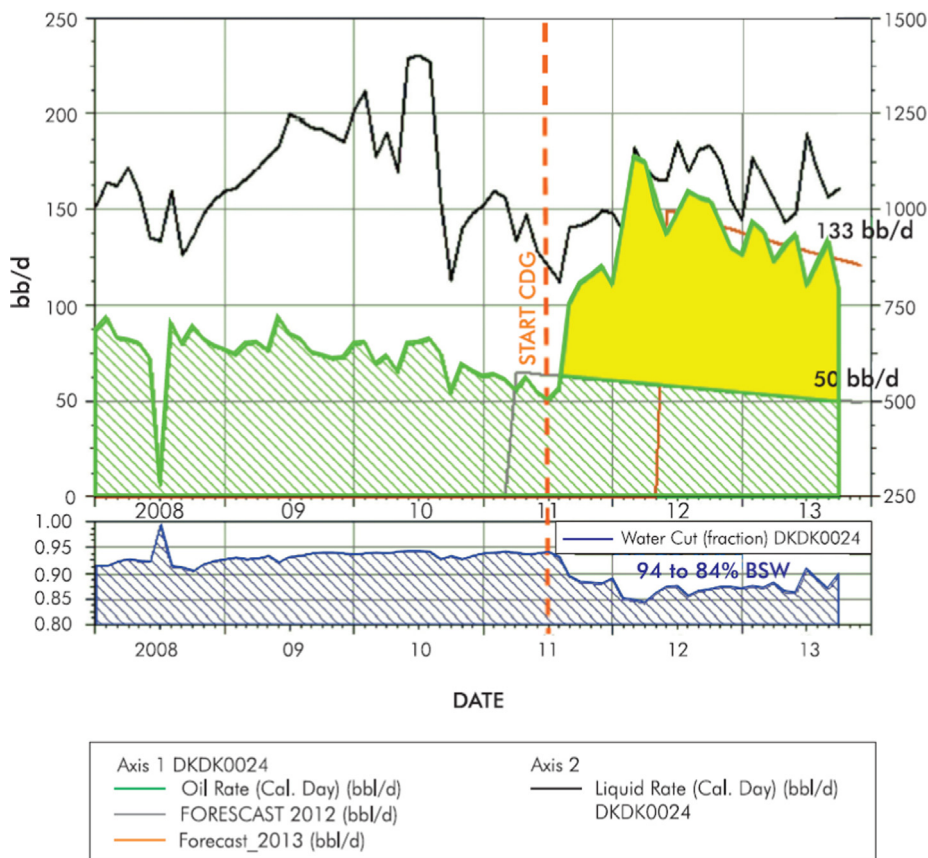
Fig. 33. Production response of well DK-24 since the CDG injection process started at well DK-3 [301].

improvement in the oil production (Fig. 33). The CDG used proved to be an efficient agent to boost the oil production, recovering up to 14.6% more oil after traditional waterflooding, using different injection schemes of HPAM and Aluminium Citrate (Fig. 34).

Regarding the economical analysis of the process, the incremental cost per barrel showed to be very similar to a traditional polymer flooding, with a final result of 4.6 U$D/bbl, which means that CDG projects could be applied with good results in heterogeneous formations.

All in all, the employment of new products may boost the productivity of chemical EOR methods. It is considered nowadays that chemical EOR processes produce approximately 500000 bbl/day, and it is foreseen that this value will increased as the oil price rises and other non-conventional sources start being exploited. Assuming an average increase in the recovery of about 20% over traditional chemical EOR

processes, this would represent an additional of 100000 bbl/day, which is roughly equal to 572 TJ/day of additional energy available. This value may be further increased if these EOR processes are boosted by means of different technologies, such as nanotechnology, altering the properties of the fluids and/or rock formation in order to increase the oil production [51].

4. Surfactant flooding

Polymer flooding is one of the most successful EOR methods acting on the viscosifying properties, but there are also other techniques focused on the phases' interfacial properties. Surfactant flooding for enhanced oil recovery is not new but have been used for more than 40 years in oil reservoirs after waterflooding became economically non-profitable [106,302–307]. Surfactant comes from the term "surface
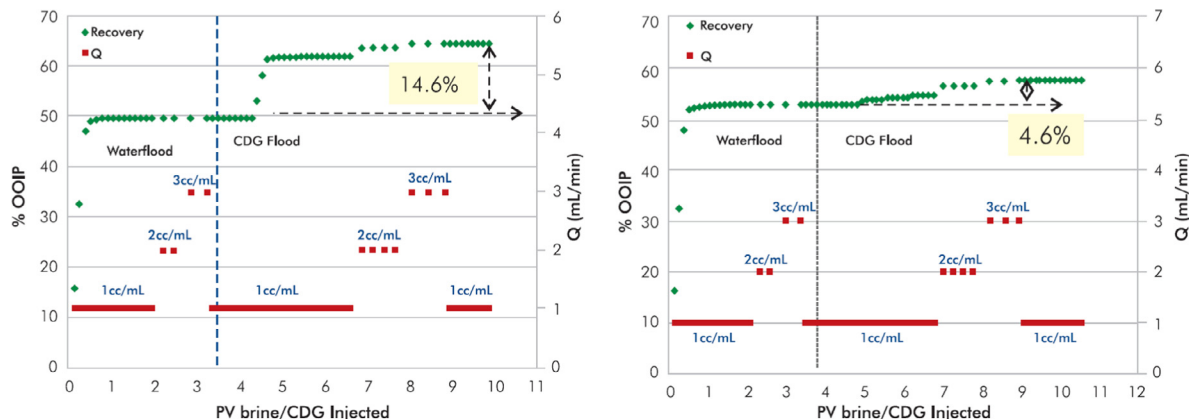
Fig. 34. Incremental recovery factor by CDG injection in Dina Cretaceous field: co-injected (left) and a week-old CDG (right) [301].

active agents" and they are amphiphilic organic compounds, made of an hydrophobic and a hydrophilic part in the same molecule [308–314]. Amphiphilic is a combination of a hydrocarbon chain that acts as hydrophobic group (the "tail") and a hydrophilic group as the polar part (also known as the "head"). Amphiphiles adsorb effectively to interfaces and typically contribute to significant reductions of the interfacial energy [315]. Hence, what makes surfactants useful in EOR is that they can be soluble in both oil and water. Surfactants can be classified according to the ionic nature of the head group in anionic, cationic, nonionic, and zwitterionic (or amphoteric) [316]. Anionic surfactants are most widely used because they present low adsorption on sandstone rocks. In the other hand, cationic surfactants can be strongly adsorbed in sandstone rocks. Then, it is generally not used in reservoirs with this lithology, but it can be used in carbonate rocks to change wettability from oil-wet to water-wet. Nonionic surfactants are primarily used as cosurfactants, which are chemicals added to enhance the effectiveness of a surfactant. Cosurfactants are often used to increase the oil-solubilizing capacity of microemulsion surfactant systems or they might also be used to improve the phase behavior [317]. These groups are more tolerant to salinity but they do not recover as much oil as the anionic ones. Zwitterionic surfactants contain two active groups together that are nonionic-anionic, nonionic-cationic, or anionic-cationic [23]. The target in designing surfactants is to achieve low IFT at low concentrations and acceptable adsorption rates [318,319]. Ultralow interfacial tensions of less than 10^{-3} mN/m have been reported with less than 0.1 wt% surfactant concentration. However, the action of the surfactant could also lead to a damage in the reservoir formation. Yuan [144] listed for this agent that surfactants can cause an excessive wettability alteration leading to a water-in-oil blockage; also, in the case of anionic surfactant with cationic fluids and minerals, this could result in the precipitation and loss of surfactant and possible block of pore throats, and finally, the excessive adsorption onto the rock formation may cause a significant loss of porosity and permeability. Table 3 presents the general screening criteria to conduct a surfactant flooding process.

The oil recovery potential by this kind of flooding and its influence on the IFT is better explained by the Capillary Desaturation Curves (CDC). These relate the ratio between the residual oil after waterflooding and residual oil after surfactant flooding as a function of the capillary number (Fig. 35), a dimensionless group expressing the proportion between capillary and interfacial forces. In a typical CDC curve, a plateau can be appreciated for both phases at low capillary numbers. These remain constant until a Critical Capillary Number (around 10^{-5} for oil) and then steadily decrease as the capillary number increases. When the capillary number is around 10^{-2}, it yields almost negligible residual oil saturation.

$$N_{vc} = \frac{v \cdot \mu}{\sigma_{ow}}$$

(4.1)

Choosing the best surfactant (Table 4) depends on the characteristics of crude oil, brine, reservoir, and several other factors, such as pressure, temperature, compatibility, and thermal and aqueous stability [271,321–327]. A successful surfactant flood should achieve sufficiently low IFT to move the trapped oil, and should maintain the stability of the surfactant slug during flooding throughout the reservoir. Thus, the deeper our knowledge is about interfacial tension behavior on the formation and movement of an oil bank, the better the EOR displacement will be, in terms of cost-effective chemical flood technologies. Nevertheless, it is important also to consider the effects of these chemical on the environment. Thus, novel amino-acid-based surfactants which are environmentally friendly are also important for the industry, such as the one presented by Madani [328], due to its biodegradability, biocompatibility, and not severe irritation and toxicity characteristics.

Also in surfactant flooding, the molecule's architecture could present great potential in EOR. As example, another kind of surfactants developed by Menger [330–333] are denominated Gemini (or dimeric)

surfactants (Figs. 36 and 37). These are composed by two amphiphiles (non-polar tail and polar head) linking the polar heads by means of a "spacer". Zana [334] and Menger [333] reported values of CMC that are one to two orders of magnitude lower than for the corresponding conventional monomeric units and also achieve lower IFT values than traditional surfactants. The spacers can be short or long methylene groups and rigid, polar and non-polar moieties might also be used as spacers [332].

This group of dimeric surfactants show good resistance and have good performance under high temperature and high salinity conditions typically encountered in oil reservoirs. They also show lower adsorption rates than conventional surfactants [271,336–338]. Moreover, Beltrán [339] and Hernández [340] developed zwitterionic Gemini surfactants intended to alter wettability in porous media in order to improve the recovery factor. Gemini surfactants present great potential to be used in oilfields where standard EOR agents are not economically profitable due to adsorption problems or interfacial phenomena.

Surfactant flooding presents several advantages in mature oilfields where the residual oil saturation have been reached and the capillary forces dominate. The modification of the interfacial properties improves the microscopic sweeping, achieving better oil recoveries. It has been reported that surfactant EOR flooding processes can improve up to 20% the recovery from standard secondary processes (Fig. 38). The main disadvantage in this process is the chemical's high adsorption rates which decrease substantially the economic efficiency of the method and that it is not applicable to medium- and high-viscosity oilfields due to unfavorable mobility ratios [341–344].

A different process with surfactant includes the use of nanoparticles as a mean to improve the oil recovery. Nanoparticles are known for slightly improving the rheological properties but more importantly for a modification of the rock's wettability, altering the relative permeabilities and thus the oil mobility (Fig. 39). The combined action of EOR agents as surfactants along with nanoparticles may significantly improve the recovery efficiency and it is considered a topic to be further investigated in order to maximize the joint efficiency of chemical EOR agents with nanotechnology [345,51].

4.1. Mechanisms of surfactant flooding

During a surfactant flooding the chemical is present on the oil/water interface as well as on the rock surface, reducing the interfacial tension, thus improving the flow capacity of the mixture. Several surfactant flooding mechanisms take place in order to improve oil recovery. Therefore, the surfactant mainly affects the microscopic efficiency by changing the rock wettability and the interfacial tension. Nevertheless, since it changes the viscosity of water due to the same principles previously commented with the polymers, affects, to a lesser extent, the

Table 3
General screening criteria for surfactant flooding processes [103,104,320].

Screening Parameter		Range/Value Recommended
Crude Oil		
Viscosity	cP	<35
Gravity	°API	>20
Composition	–	Light, intermediates preferred
Reservoir		
Type of Formation	–	Sandstones preferred
Depth	m	<2,800 (due to thermal restrictions)
Temperature	°C	<95
Net Thickness	m	Not critical
Initial Reservoir Pressure	MPa	Not critical
Porosity	%	Not critical
Permeability	mD	>10
Initial Oil Saturation	% PV	>35
TDS	ppm	<50,000
Total Divalent Cations	ppm	Not critical
Special Remarks	–	–
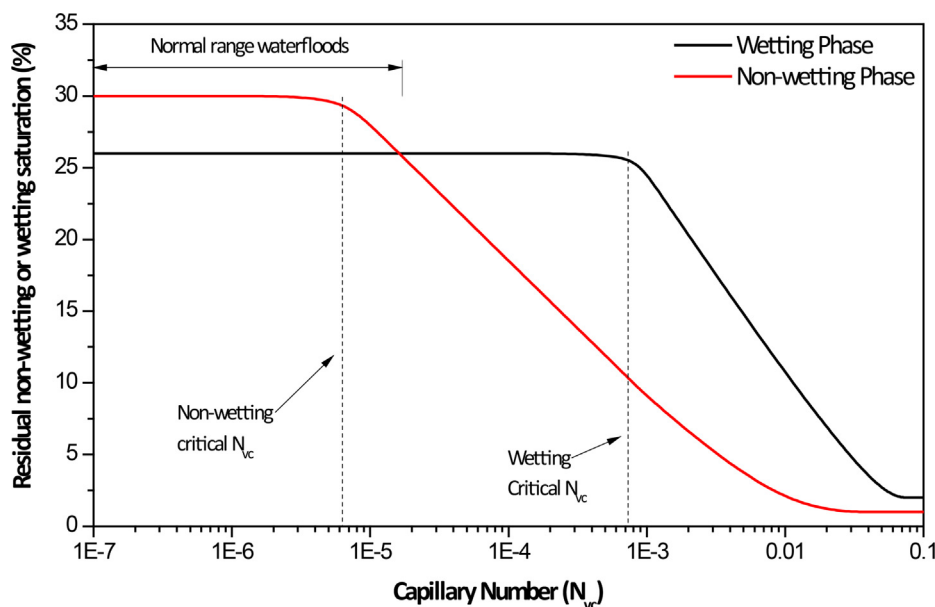
Fig. 35. Schematic capillary desaturation curve for wetting and non-wetting phases [23].

macroscopic efficiency by reducing the mobility ratio [320].

4.1.1. Reducing the Oil-Water IFT

After waterflooding, globules of oil are left trapped in the reservoir due to capillary forces (Fig. 26). When surfactant is injected, it is adsorbed onto, or concentrated at a surface or oil/water interface, increasing the capillary number. Increase of the latter, caused by a decrease of the IFT, makes residual oil globules trapped in the rock pores to flow [346–351].

The surfactant concentration is a factor to be taken into account. When an anionic surfactant is dissolved in aqueous solution, it dissociates into a cation and a monomer (what happens also at low surfactant concentrations). As the concentration is increased, the lipophilic parts of the surfactant will begin to associate among themselves to form what is called micelles (groups of monomers) (Fig. 40). A plot of monomer versus surfactant concentration is then a curve beginning at the origin, increasing monotonically, reaching a level called critical micelle concentration (CMC) and then leveling [23]. Therefore, below the CMC, the IFT decreases steadily along with the increasing surfactant concentration, but after the CMC, IFT stays steady or slightly increases with the concentration.

The capillary number is usually in the range $10^{-8} \sim 10^{-7}$ in
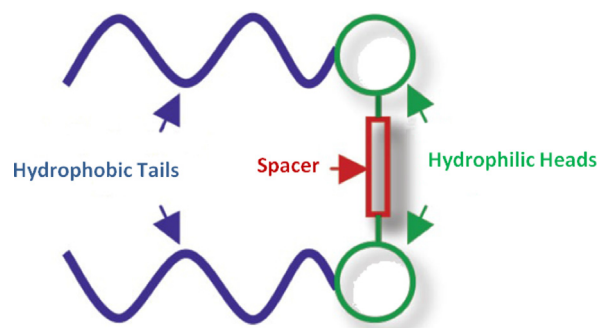
Fig. 36. Schematic representation of a gemini surfactant [335].

waterflooding. It can be appreciated in Fig. 35 that when it is around 10^{-3}, oil recovery should be roughly 100%. The oil-water interfacial tension is usually $20 \sim 50$ mN/m, and with an ideal surfactant it could be as low as $10^{-2} \sim 10^{-3}$ mN/m, making the capillary action almost negligible, decreasing the residual oil.

Table 4
Surfactant classification [329].

Class	Examples	Structures	Schematic Representation
Anionic	Sodium stearate Sodium dodecyl sulfate Sodium dodecyl benzene sulfonate	$CH_3(CH_2)_{16}COO^-Na^+$ $CH_3(CH_2)_{11}SO_4^-Na^+$ $CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$	Hydrophobe ◀▶ Hydrophile
Cationic	Laurylamine hydrochloride Trimethyl dodecylammonium chloride Cetyl trimethylammonium bromide	$CH_3(CH_2)_{11}NH_3^+Cl^-$ $C_{12}H_{25}N^+(CH_3)_3Cl^-$ $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	Hydrophobe ◀▶ Hydrophile
Nonionic	Polyoxyethylene alcohol Alkylphenol ethoxylate Alkyl Polyglucosides	$C_nH_{2n+1}(OCH_2CH_2)_mOH$ $C_9H_{19}-C_6H_4-(OCH_2CH_2)_nOH$ $C_nH_{2n+1}O(C_6H_{10})_mH$	Hydrophobe ◀▶ Hydrophile
Zwitterionic	Dodecyl betaine Lauramidopropyl beatine Alkyl-hydroxyl-sulfobetaine	$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$ $C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$ $C_nH_{2n+1}N^+CH_2CH(OH)CH_2SO_3^-$	Hydrophobe ◀▶ Hydrophile
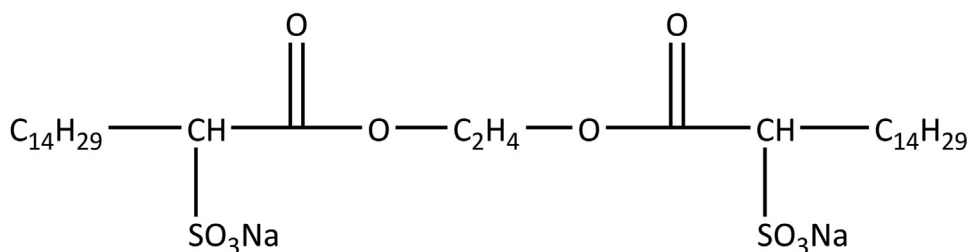
Fig. 37. Gemini surfactant – anionic DMES-14 [271].
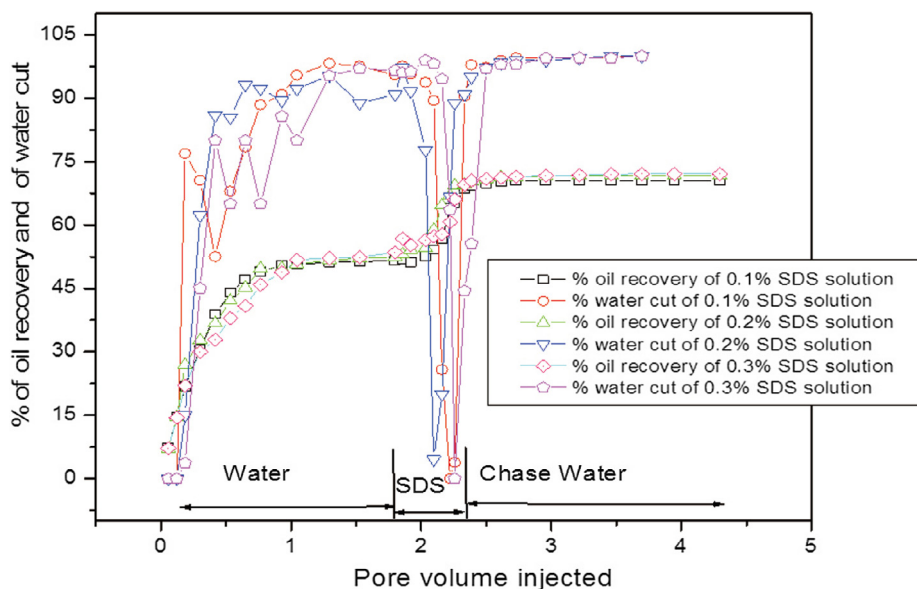
Fig. 38. Production performance of SDS flooding at different concentrations [343].

4.1.2. Emulsification mechanism

Emulsions can be defined as dispersions of one liquid into another one, immiscible with the first [353]. The liquid droplets (the disperse phase) are dispersed in a liquid medium (the continuous phase). A third component is required to disperse two immiscible liquids, which is known as the emulsifier. The choice of the latter is important for both the formation of the emulsion and also for its long-term stability. Alvarado [354] studied the role of this third component in the generation and stability of the emulsion. Kumar [353] considered that the emulsifier should both decrease the interfacial tension between the two immiscible liquids and stabilize the generated interface against forces of coalescence. There are three main criteria necessary for the formation of a crude oil emulsion:[351,355,356] Two immiscible liquids in contact, surface active component must present as the emulsifying agent (emulsifier), and enough energy in the form of a mixing or agitating effect so as to disperse one liquid into another as droplets.

Emulsification of the oil phase is one important mechanism in chemical EOR with surfactants. The surfactant scales off oil from rock surface forming an emulsion reducing the oil viscosity and altering the rock wettability, thus improving mobility ratio and macroscopic efficiency [357–361]. Surfactants are adsorbed onto the oil/water interface providing a protective barrier around the oil dispersed droplets. Moreover, surfactants stabilize the emulsion by reducing the interfacial tension of the system as well as they improve stability by giving an electrical charge on the droplet surface, thus reducing the physical contact between the oil droplets, decreasing the probability of occurrence of coalescence events, as described by Perazzo [362].

4.1.3. Wettability mechanisms (oil-wet to water-wet)

The microscopic displacement efficiency is closely related to rock wettability (Fig. 41). Oil-wet surface results in poor displacement efficiency, whilst water-wet one provides the best outcomes. The surfactant might increase the contact angle of wettability between oil and rock, making the rock surface changing from oil- to water-wet. The final result of this physical process is reducing the adhesion energy of oil on rock surface [363–366].

4.1.4. Phase equilibrium and the effect of salinity in surfactant flooding

In surfactant EOR flooding, the phase behavior and the phase equilibrium between the displacing and the displaced fluids very likely will affect the recovery efficiency. Considering the surfactant phase behavior, typically three systems are mentioned, based on the work developed by Winsor [368]. Winsor II($-$) are systems where the multiphase region has lower-phase microemulsion (oil-in-water) in equilibrium with excess of oil. The Winsor II($+$) systems are upper-phase microemulsions (water-in-oil) in equilibrium with excess of water or brine. Winsor III systems exhibit a middle phase microemulsion, creating a three phase system (Fig. 42) as described and studied by Hirasaki [308,369,370], Larson [371–373] and several authors [374–379].

As it was previously mentioned, surfactant reduces IFT between oil and water, making the trapped oil in the reservoir to mobilize. The reduction in IFT depends upon a number of factors including, among others: surfactant concentration, type of oil in the reservoir, the brine salinity and the amount of surfactant lost into the rock formation due to adsorption (which also is function of the lithology of the reservoir) [351].

In terms of brine salinity, at low values is called under optimum (Winsor Type II-) when the surfactant is in the aqueous phase. On the other hand, at high salinities is called over-optimum (Winsor Type II
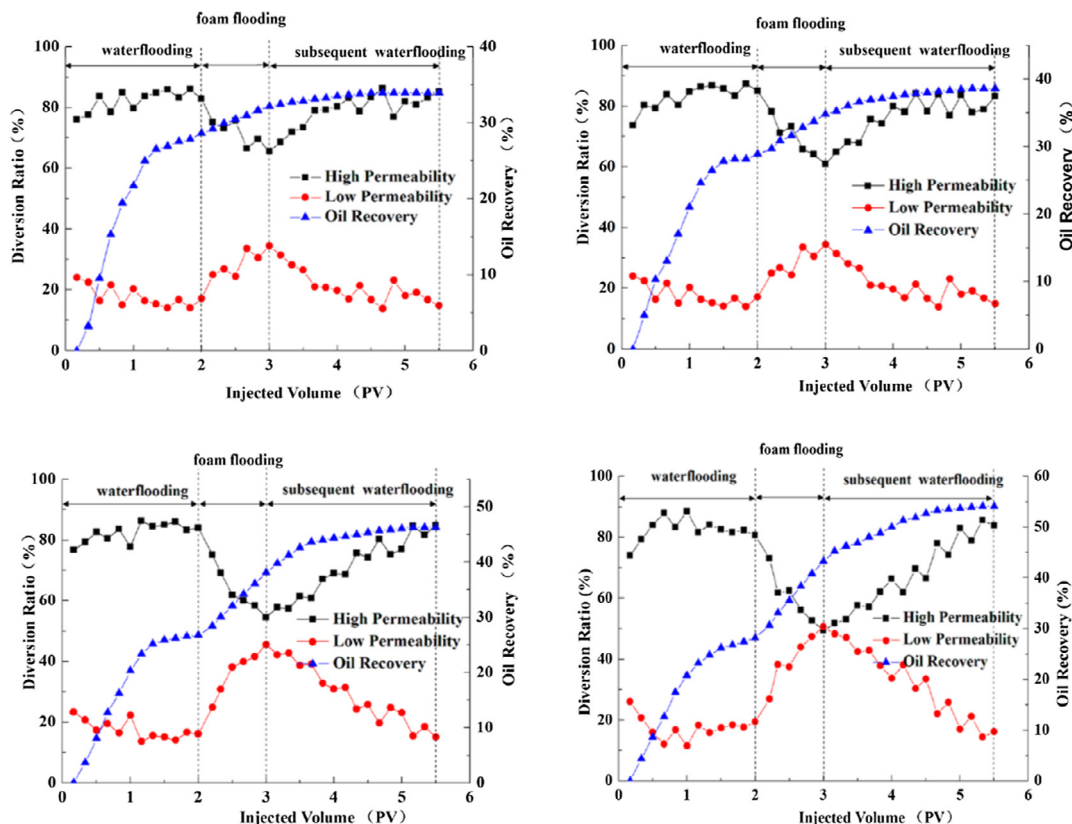
Fig. 39. Change of diversion ratio and oil recovery performance during different foam flooding processes as a function of SiO$_2$ concentration: 0.0 wt% SiO$_2$ + 0.5 wt% SDS (top left); 0.1 wt% SiO$_2$ + 0.5 wt% SDS (top right); 0.5 wt% SiO$_2$ + 0.5 wt% SDS (bottom left); 1.0 wt% SiO$_2$ + 0.5 wt% SDS (bottom right) [345].

+), when it will go preferentially into the oleous phase. At intermediate values, the third phase appears in the system and this condition (Winsor Type III) results in the lowest IFT, and then it should represent the optimal condition for a surfactant flooding [370,380]. Gupta and Trushenski [381] showed that, at low salinities relative to optimal value, surfactant retention was small but also the oil recovery was poor. At high salinities, the latter also rendered low results because of high surfactant retention. So, the optimal recovery occurred at a salinity where IFT was low enough but surfactant retention was not too high.

4.2. Adsorption

Loss of surfactants because of their interactions with reservoir rocks is one of the most important factors determining the efficiency of a flooding technique [382]. Adsorption is a process where surfactant aggregates and micelles deposit onto the rock surface. In general, adsorption is governed by a number of forces such as covalent and/or hydrogen bonding, electrostatic attraction, or non-polar interactions between the adsorbed species, among others [383]. This phenomenon will cause a loss of surfactant due to adsorption and retention in the porous media. The adsorption isotherm is rather dependent on the type of surfactant, the length of the chain, the temperature, the characteristics of the rock and the type of electrolytes present in the solution [310,382,384–390]. Saxena [391] found a direct relationship between salinity and the adsorption of anionic surfactants, which was decreased with the presence of alkali and nanoparticles.

The mechanisms involved in this process can be listed as:[392] ion exchange and/or pairing, hydrophobic bonding, adsorption by
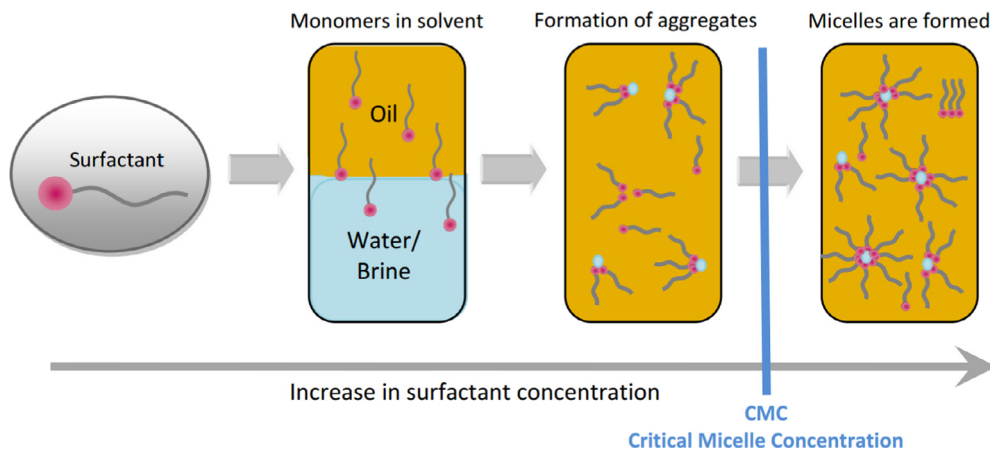
Fig. 40. Micelle formation in water-in-oil (w/o) emulsions [352].
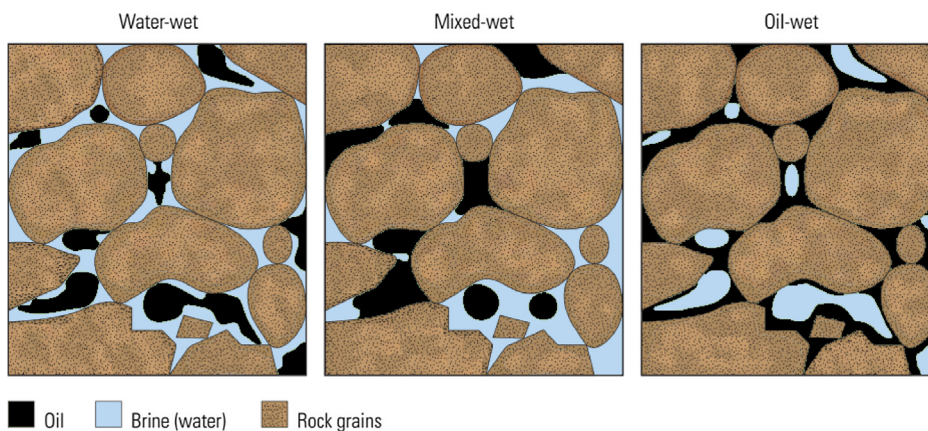
Fig. 41. Different wettability schemes in porous media [367].

polarization in surfactant with aromatic nuclei, and adsorption by dispersion forces. The process starts with aggregates formed at the surface. A layer forms and when the equilibrium monolayer adsorption has been reached, the system will form an extra layer, which is the origin of significant surfactant losses (Fig. 43) [352,392].

5. Polymeric surfactants

A relatively new development based on the agents previously mentioned was the synthesis of a novel group of functional polymers known as polymeric surfactants. They combine the characteristics of viscosifying and reducing mobility of traditional polymers solutions, together with hydrophilic and hydrophobic groups attached in the chemical structure, which combined with the hydrophobic/hydrophilic

polymer chain, create also a surfactant, increasing the mobility by means of decreasing the interfacial tension and capillary forces in the reservoir [393].

Nonetheless, a brief analysis should be made beforehand about polymeric surfactants and hydrophobically modified polymers. Both share the same key feature, this is, they are both amphiphiles, with hydrophobic and hydrophilic groups. The difference lies in the structure, and number, of these groups. According to Wever [73], the hydrophobically associative polymers (HAP) are composed by a small number of hydrophobic groups (8–18 carbon atoms moieties) distributed along the main backbone. These groups can be positioned randomly or blockwise, and coupled at one or both ends. Sheng [70] defined hydrophobically associating water soluble polymers to those which contain water-soluble monomers and a small fraction (0.5–4%)
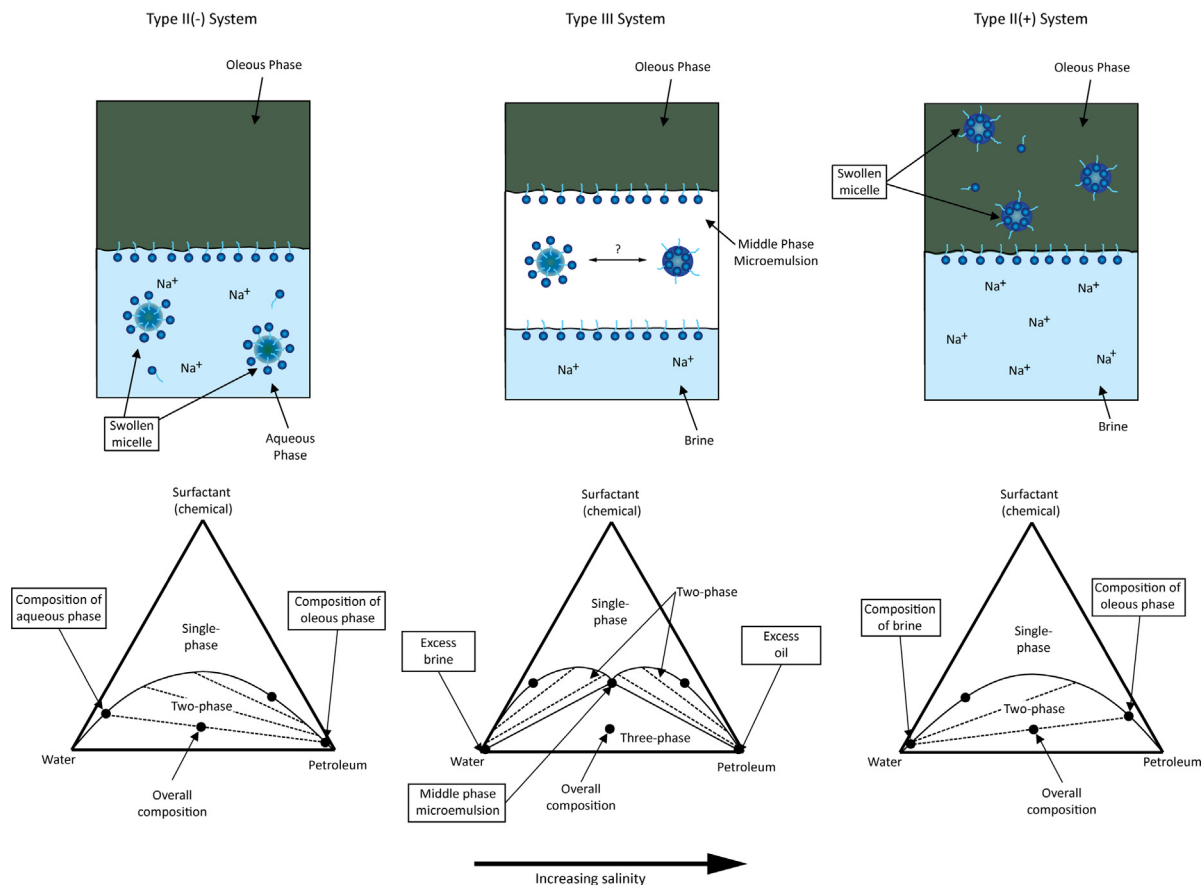
Fig. 42. Possible solubility configurations for a three component system (adapted from Lake [23]).
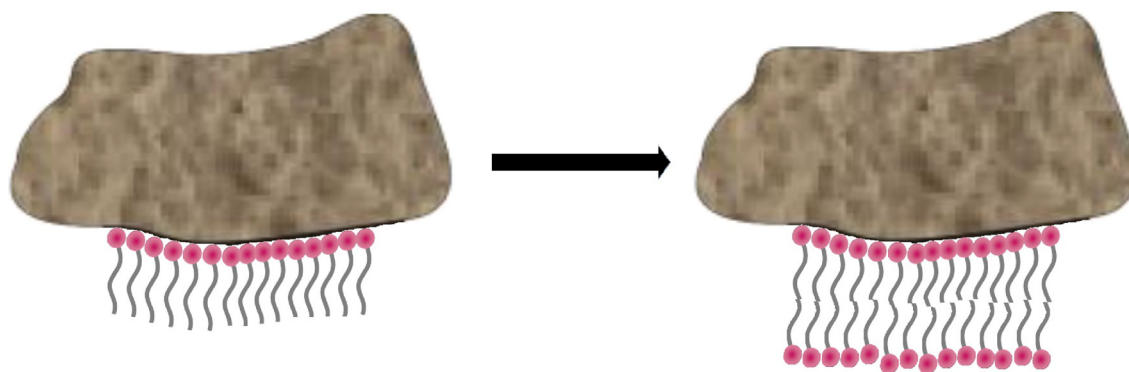
Fig. 43. Surfactant adsorption mechanism in porous media, first monolayer (left) and then becoming multilayer (right).

of water-insoluble monomers. On the other hand, polymeric surfactants may contain both the hydrophilic and hydrophobic groups within the same monomeric unit or may be formed as copolymers of hydrophilic and hydrophobic monomers. This means that the latter are not be arranged in the same ways as in HAP's, with higher content of water-insoluble monomers.

Raffa [394] introduced the different polymeric surfactants and their application in industry. He classified these molecules according to a structural point of view, depending on the relative arrangement of hydrophilic and lipophilic parts (Fig. 44). If there are present repeating units of intrinsically amphiphilic monomers, these are referred to as polysoaps, whilst polymers in which there is a clear separation between the two parts are called macrosurfactants.

These polymers can be built in three different ways: hydrophobic chains grafted to a hydrophilic backbone; with hydrophilic chains grafted to a hydrophobic backbone; and alternating hydrophilic and hydrophobic units [360].

An example of polymeric surfactant was synthesized by Abdala Elraies [264] and Pal [395], combining a sulfonate group to a hydrophobic group of an associative polymer chain (polymeric methyl ester sulfonate or PMES). Results showed that the PMES particles were found in an agglomerated form and its shape was dependent on the acrylamide content, from a spherical to a rod-like as the presence of the latter was increased (Fig. 45). Another example of polymeric surfactant was synthesized by Cao [396] using surfactants based on carboxy methyl cellulose and alkyl poly(etheroxy) acrylate. He also analyzed as well the effect of salt, alcohol and alkali on the interfacial tension properties. Also, Jinhong Sun [397] developed an amphiphilic polymer by radical

copolymerization of acrylamide, dodecyl polyoxyethylene acrylate (DPEA) and N-(1,1,3,3-tetramethyl butyl) acrylamide (TBA) analyzing by several methods its emulsification properties. Ke-Liang Wang [398] reported that some functional groups have been grafted to hydrocarbon main chains to form a multivariate graft copolymer, called functional polymer surfactant (also referred to as polymeric surfactant) [399,400]. This represented a new type of polymer working as a single displacement agent, but having viscosifying properties as a polymer and acting as a surface active agent like surfactants, improving its solubilization and emulsification capacity of crude oil. Furthermore, this new polymer altered the rock wettability, changing it to water-wet. Ke-Liang presented this new polymeric surfactant as an alternative where reservoirs have entered in high water cut stage and conventional polymers could not meet the requirements of EOR and used the Daqing Oilfield as trial field test for this research (Fig. 46). An interesting alternative for EOR applications may be the combination of the amphiphilic polymers using a star-like architecture with nanoparticles, such as presented by Liu [401]. The molecule's architecture is a core of nano-SiO$_2$, hyperbranched polyamidoame as the subshell, and amphiphilic polyacrylamide (twin-tailed octyl chains as hydrophobic moieties, and amide/carboxyl groups as the hydrophilic moieties) as the shell. Even though the interfacial properties of the molecule were not reported, the increased viscoelastic properties achieved a better recovery efficiency when compared to traditional polymer flooding.

Another type of polymeric surfactants was developed by Raffa [402–404], creating amphiphilic block copolymers using ATRP. The block copolymers had the following schematic structures: AB diblock and ABA triblock (Figs. 47 and 48). Moreover, triblock copolymers with
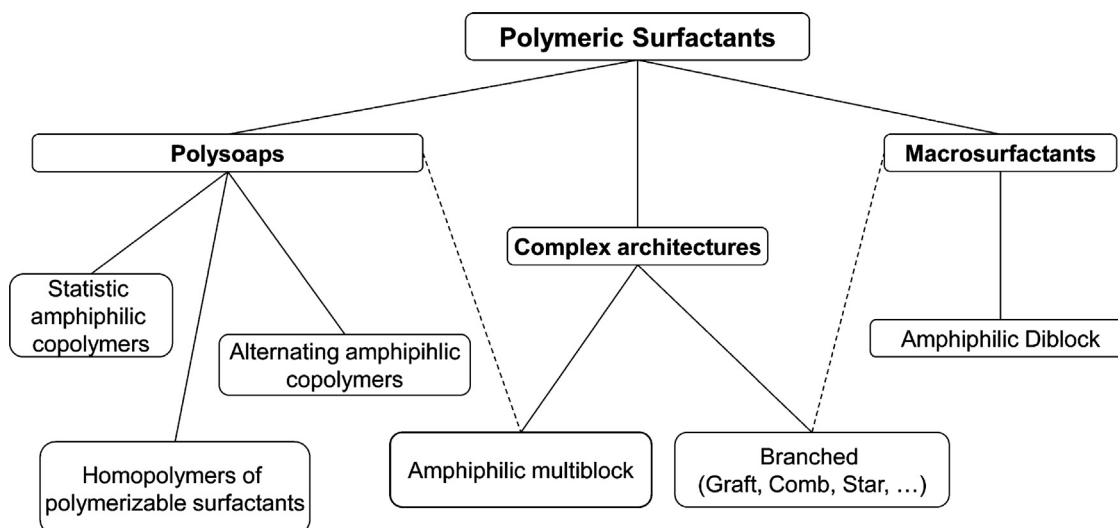
Fig. 44. Classification of polymeric surfactants [394].
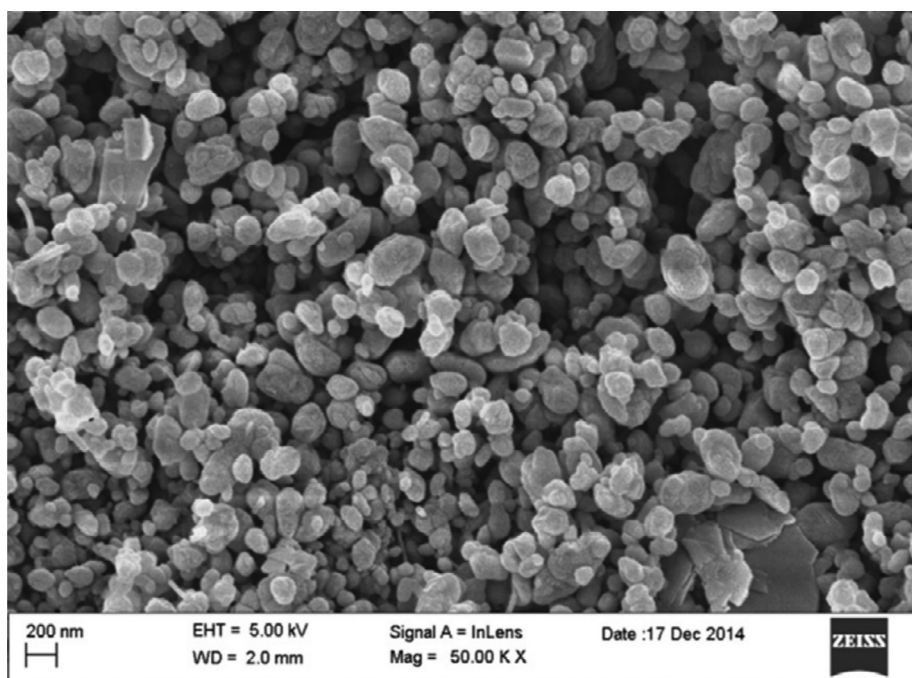
Fig. 45. Field emission scanning electron microscopy of the PMES polymeric surfactant developed by Pal [395].
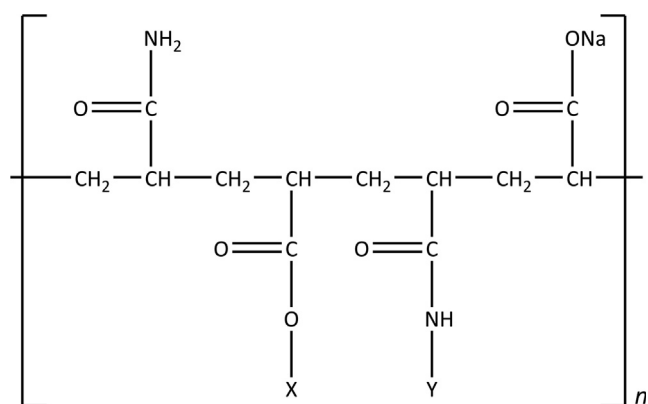
Fig. 46. Polymeric surfactant used in Daqing oilfield where X and Y represent one of the following functional groups: -OR, -NHR, -RSO$_3$Na, quaternary ammonium surfactant unit, cationic Gemini units or -RSH [398].

Fig. 47. Representation of different copolymer architectures where (A) represents a random copolymer, (B) a diblock copolymer, (C) a triblock copolymer, (D) a graft copolymer and (E) a star copolymer [414].

similar (ABA) or different (ABC) end blocks were also studied for EOR purposes [405–408]. In these, the hydrophilic block B was by polyethylene oxide (PEO) or polyacrylic acid (PAA), and the hydrophobic blocks by polystyrene or aliphatic alkyl chains. The rheological properties were also studied, evidencing a non-Newtonian behavior, fitting the Power Law fluid model. Also, he pointed out that the addition of surfactants also had an influence on the rheological behavior of these copolymers [408–413].

Due to the presence of hydrophilic and hydrophobic groups, polymeric surfactants present a wide variety of micelles and similar structures [394]. These kinds of polymers form viscoelastic solutions that present a transition to gels at a certain critical concentration, depending on the composition and the copolymer's architecture [394]. The influence of these structures in the rheology of the solution is showed in Figs. 49 and 50. According to the theory, in the dilute phase the molecules of the polymer do not interact with each other, until the overlapping concentration is reached (c∗). Above c∗, in the semi-diluted regime, the viscosity starts to increase sharply as the polymer coils start to interpenetrate and shrink. Then, with subsequent increase of volume fraction the threshold for gelation is reached in the concentrated regime

(section **c** of Fig. 49). However, this regime is not recommended for EOR applications in low- and medium-permeability fields since the pressures drops may exceed the allowable limits [415,416].

This new group of functional polymer units represented a breakthrough, tackling some of the problems detected in surfactant and polymer flooding, for instance, their ability to form shear-dependent transient association in water with subsequent shear-thickening behavior at high salt concentrations and in extensional flow [394]. This yields an increase in oil recoveries compared with conventional secondary or polymer flooding processes due to the enhanced rheological and viscoelastic properties, creating a complex stress field which improves the microscopic sweeping efficiency (up to a 30% with respect to conventional waterflooding) [418–420]. However, there is still much research to be done in the application of polymeric surfactant with different EOR agents (combined recovery techniques), such as
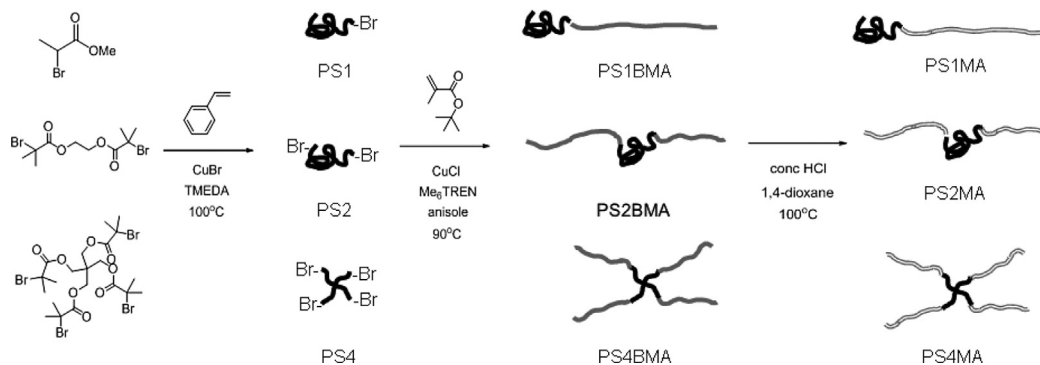
Fig. 48. Several diblock, triblock and star polymeric surfactant structures [403].

rheological and interfacial properties. All things considered, the use of polymeric surfactants might represent a way to boost the oil recovery factors in chemical EOR (Fig. 51) [421–423].

6. Chemical EOR combined techniques

During this review the basic methods of enhanced oil recovery were presented and discussed, along with their mechanisms and the most common chemical agents used. The properties of polymers and surfactants have also been discussed as well as the development of new products and trends. Nevertheless, more complex methods have been developed, combining one or more of the traditional systems, resulting in a whole new range of procedures [424]. This is how, among others, the following processes were developed: Surfactant-Polymer (SP), Alkaline-Surfactant (AS), Alkaline-Polymer (AP), Alkaline-Polymeric Surfactant (APS), Alkaline-Surfactant-Polymer (ASP), Polymer-Alternating-Gas (PAG) or Surfactant-Alternating-Gas (SAG or FAWAG), and Alkaline-Surfactant-Alternating-Gas (ASAG) [63,64,70,425–427]. These combined techniques report higher recoveries not only as a result of a linear combination of the advantages of the EOR agents injected, but also because of their synergy acting together in porous media, which improves the sweeping efficiency (Fig. 52).

Combined chemical EOR processes can be also developed from the action of gases with chemical agents, a process derived from WAG (Water Alternating Gas). WAG consists in the injection of slugs of water alternately with gas, even though sometimes the two fluids are injected simultaneously (SWAG). Injecting water alternately with the gas reduces the volume of gas required to maintain reservoir pressure and it also reduces the tendency for the gas to finger or channel through the
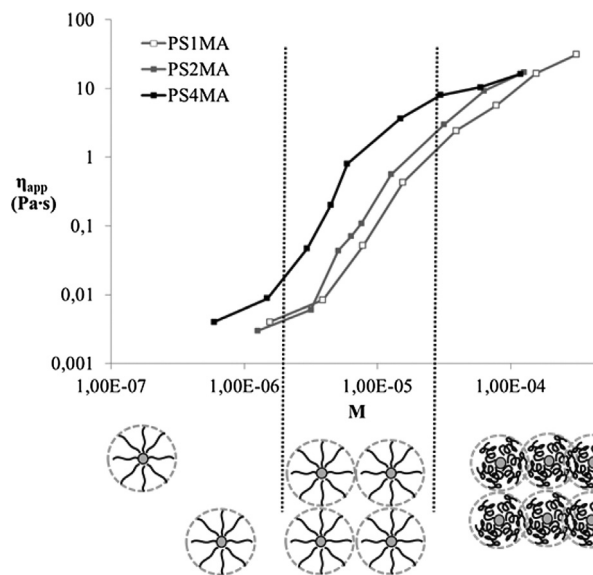
Fig. 50. Apparent viscosity ($\dot{\gamma} = 1\,\mathrm{s}^{-1}$) as a function of concentration and schematic representation of micelles overlapping and shrinking in the different regions [373].

oil as the presence of mobile water in the pore space reduces the gas mobility through relative permeability effects. Vertical sweep efficiency is also improved as water, being heavier than oil, tends to slump towards the bottom of the reservoir while the gas, being lighter, rises to
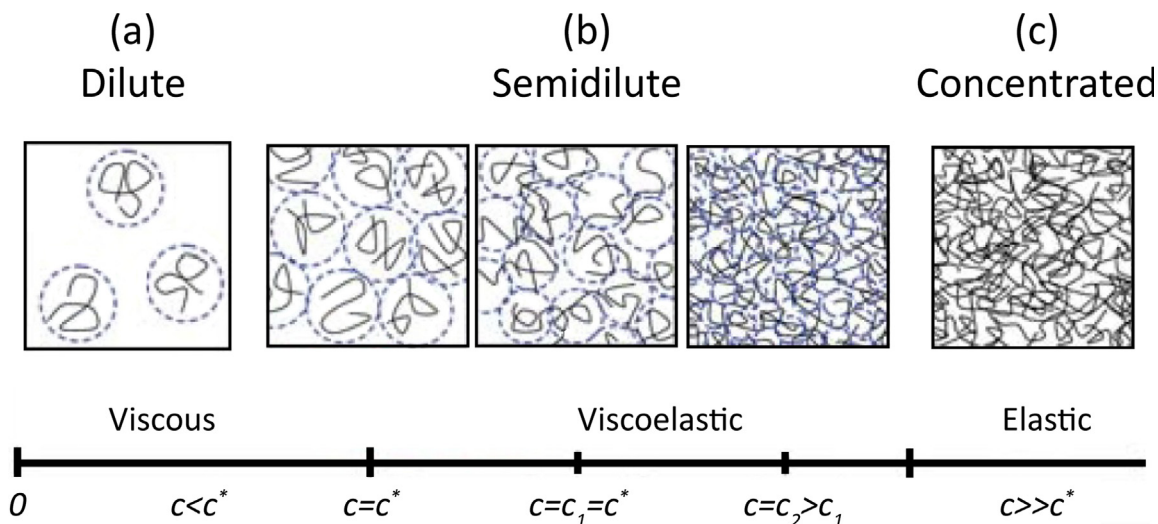
Fig. 49. Behavior of polymer solutions as the concentration of polymer increases [417].
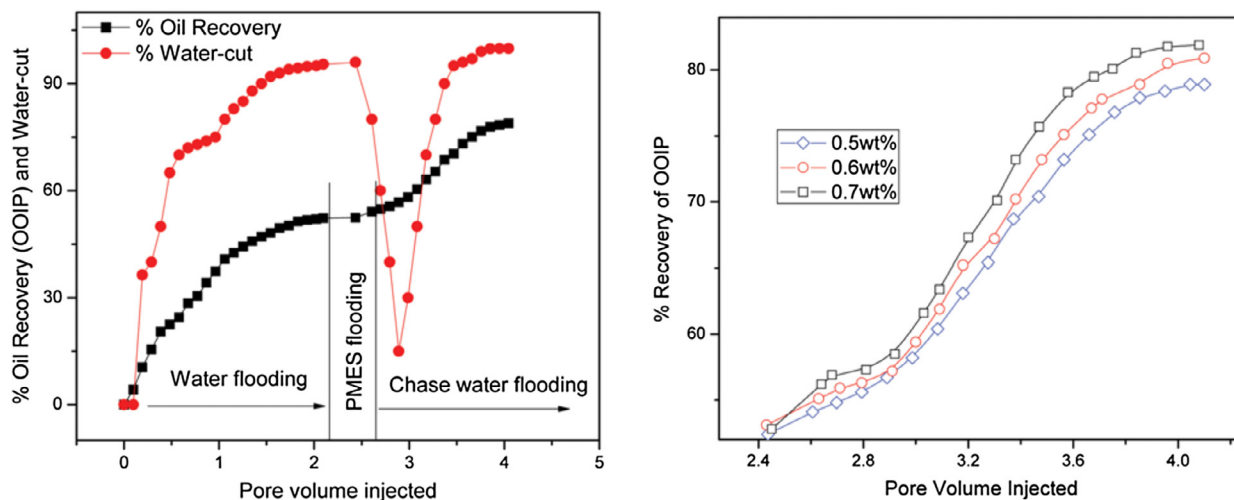
Fig. 51. Oil recovery and water cut as a function of the injected pore volume for a polymeric surfactant flooding with Polymeric methyl ester sulfonate (PMES) (left) and comparison of enhanced oil recovery with different concentrations of PMES (right) [421].

the top [50,428–436]. Therefore, Surfactant (SAG) and Polymer Alternating Gas (PAG) combine the characteristics recently mentioned with the properties of surfactants and polymers, respectively [437]. This is the reason why these processes are also called chemically enhanced Water Alternating Gas methods [363,438–449]. However, these are just recent developments, so it is considered that further research must be carried out in the laboratory as well as in field pilot tests to validate the results obtained so far.

6.1. Alkaline-Surfactant-Polymer (ASP)

This EOR process was created combining three different chemical species. ASP flooding consists in injecting, before the surfactant and polymer slugs, alkaline or caustic solutions into the reservoir. Common chemicals used as alkaline injection products are sodium hydroxide, sodium metaborate, sodium silicate, or sodium bi/carbonate [59,450]. However, Berger [451], Gong [452], Zhao [453], and Bataweel [454,455] reported also the use of organic alkalis as a medium to improve the more traditional inorganic ones (Fig. 53). The effects of organic alkali on IFT, adsorption and viscosity were compared with those from the results of conventional inorganic alkalis. The organic alkali

was found to be suitable with high TDS (including high hardness concentration) brines. They can be used without the need of water softening and in some cases they provide better results than conventional alkali in systems where both can be used. Major advantages of these products are the non-toxicity and biodegradability.

Something important to be taken into account is that these caustic chemicals react with the natural acids (naphtenic acids) present in crude oils to form surfactants in-situ (sodium naphthenate). These in-situ generated products have the same effect as the injected synthetic surfactants displacing additional oil to the producing wells. Moreover, the alkalis also react with water present in reservoir and with the rock formation, altering the wettability. In case of alkalis, these can also damage the rock formation. Yuan [144] identified these problems as the migration and blockage of fine particles, since alkali can dissolve clays and other minerals found in the reservoir and this cause a migration and blockage of the pore throats; and also the formation of scales, which will be discussed in Section 6.1.2. The screening criteria for ASP processes is presented in Table 5.

Alkaline-Surfactant-Polymer (ASP) flooding aims at improving both microscopic and macroscopic displacement efficiencies (Fig. 54). The former is increased by reducing the IFT between water and oil through
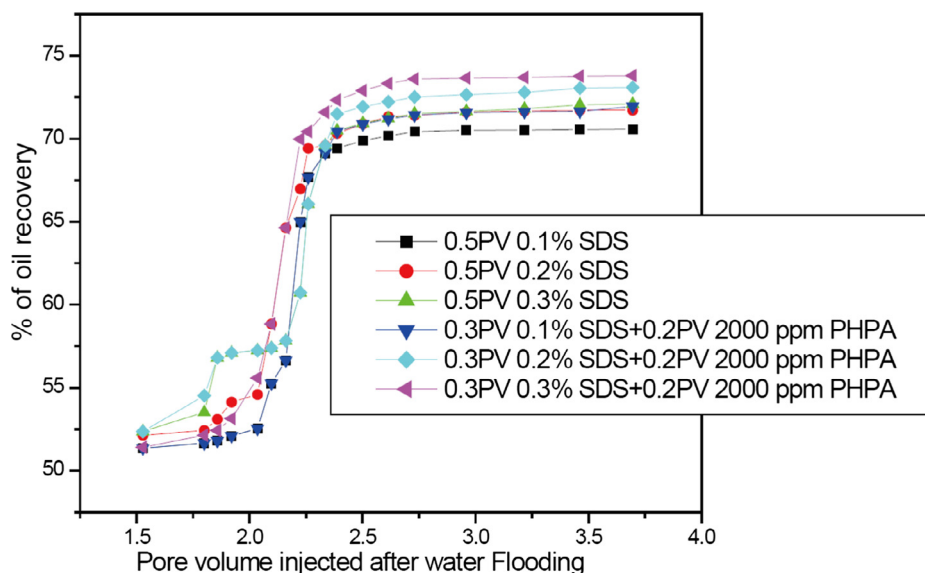
Fig. 52. Oil recovery comparison between standard surfactant EOR and a SP flooding [343].
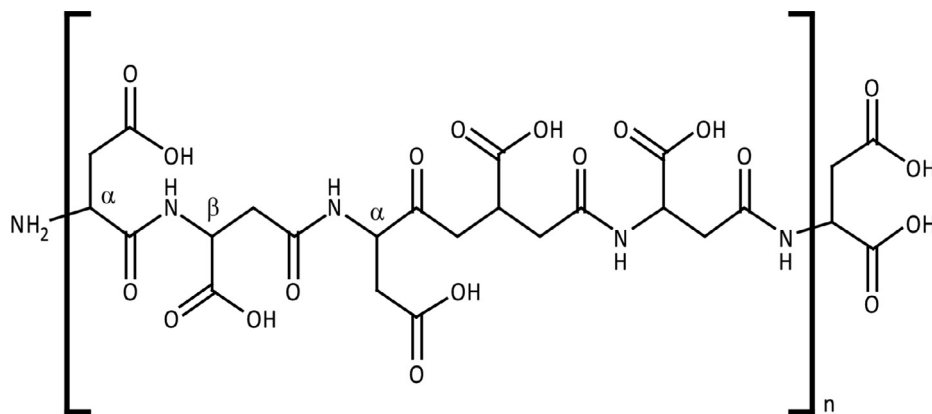
Fig. 53. Organic alkali (polyaspartic acid) chemical structure [451].

Table 5
General screening criteria for ASP flooding processes [103,104].

Screening Parameter		Range/Value Recommended
Crude Oil		
Viscosity	cP	<50
Gravity	°API	>20
Composition	–	Light & intermediates/organic acids preferred (A)
Reservoir		
Type of Formation	–	Sandstones preferred
Depth	m	<2,800 (due to thermal restrictions)
Temperature	°C	<95
Net Thickness	m	Not critical
Initial Reservoir Pressure	MPa	Not critical
Porosity	%	Not critical
Permeability	mD	>50
Initial Oil Saturation	% PV	>30
TDS	ppm	<50,000
Total Divalent Cations	ppm	<100 (to prevent scale formation)
Special Remarks	–	Low Ca clay content

the addition of a surfactant to the water and taking advantage of the viscoelastic properties of the polymers. The latter reduces the oil and water mobility ratio through its viscosifying properties [308,456]. Technical difficulties might arise due to the fact that the chemical mix needs to be carefully designed for the fluids (i.e. oil and brine) encountered in the reservoir [457]. It has been observed in this respect that ASP flooding works best with relatively low-salinity water [57].

A key factor in an ASP flooding is the synergy between the in-situ soap generated by the alkali and the injected surfactant. The optimum salinity for the former is generally ultra-low, which is in most cases unfeasible. To meet this requirement, the total injected alkali must remain lower than the total consumption amount; therefore the alkali will not propagate. In order to tackle this, the surfactant is added because the optimum salinity for the latter is higher than in the case of the soap. When both chemicals are mixed in the reservoir, the salinity range in which IFT reaches its lowest value is both increased and widened [63,458].

Furthermore, Hou [460] examined the relationship between the viscoelasticity of the polymer solution and the alkali concentration. He showed that the latter had a negative effect on the viscoelastic properties (decrease in the storage and loss modulus), affecting negatively the recovery efficiency. Despite these difficulties, ASP flooding was applied onshore in the early 1980s when the oil price was high. Recently, there has been a recent resurgence of interest as oil prices have been steadily increasing to the point where the process became again profitable. However, the only recent large field-scale application outside Daqing in China [461–463] is in Oman [464]. Several smaller ASP oilfield applications are also studied in the literature

[63,70,450,465–470]. In Daqing the pilot tests reported oil recoveries were increased by 21 to 24 % OOIP using ASP flooding over waterflooding [471–478]. In the recent years, a significant progress has been made in both laboratory studies and pilot tests to show the potential of ASP projects in mature oilfields [322,454,460,469,472,479–486]. All these field applications have shown improved recovery capabilities over secondary, polymer or even other chemical combined EOR processes (Fig. 55), with the main ASP project being carried out in Daqing (China) [481,487–489]. The advantage of ASP consists mainly in combining the different agents as well as the synergy of these working together, which improves the recovery factor between 10 to 25% with respect to secondary processes. From an economic point of view, combined techniques imply higher costs, with values ranging from U$D 6 to 11 per additional barrel, only for the products themselves. Nevertheless, considering the current and prospective energetic situation, it is forecast that the number of combined chemical projects will increase in the upcoming years [63].

6.1.1. Mechanisms of alkaline flooding

Since the mechanisms for polymer and surfactant have been previously analyzed, only those for alkaline flooding will be discussed in this section. The first one is that a surfactant (called "in-situ" to differentiate it from an injected synthetic surfactant) is generated in the reservoir when the alkaline solution reacts with the acid component in the crude oil (Fig. 56). The reaction equation yields [70],

$$HA + OH^- \rightarrow A^- + H_2O \tag{6.1}$$

where HA is an acid-like compound and A^- is the soap component. Moreover, when an alkali is added with a surfactant like in an ASP process, the alkali will reduce the adsorption of surfactant on the grain surfaces through the formation and sequestering of divalents ions [59]. Alkali is also added to the water in order to control the local salinity to ensure minimum IFT and it can also alter the rock wettability [308,490–492]. This makes surfactant work more efficiently, hence its injected amount is decreased. Other mechanisms include emulsification, oil entrainment, bubble entrapment and wettability reversal [57,63,450,493–495]. Nevertheless, the alkaline solution also reacts with the rock and connate water in the reservoir. The most important of these three set of chemical reactions in terms of alkaline mass involved is the reaction with the rock (Table 6).

6.1.2. Scaling formation

One of the major problems in ASP process is the scale formation. The alkali reacts with the rock and increases the concentration of scaling ions in the porous media, such as Ca^{2+}, Mg^{2+}, Al^{3+}, $(OH)^-$, $(CO_3)^{2-}$, $(SO_4)^{2-}$ or $(SiO_3)^{2-}$. When these ions react, they produce several inorganic scales, precipitating and depositing in production facilities as well as causing formation damage
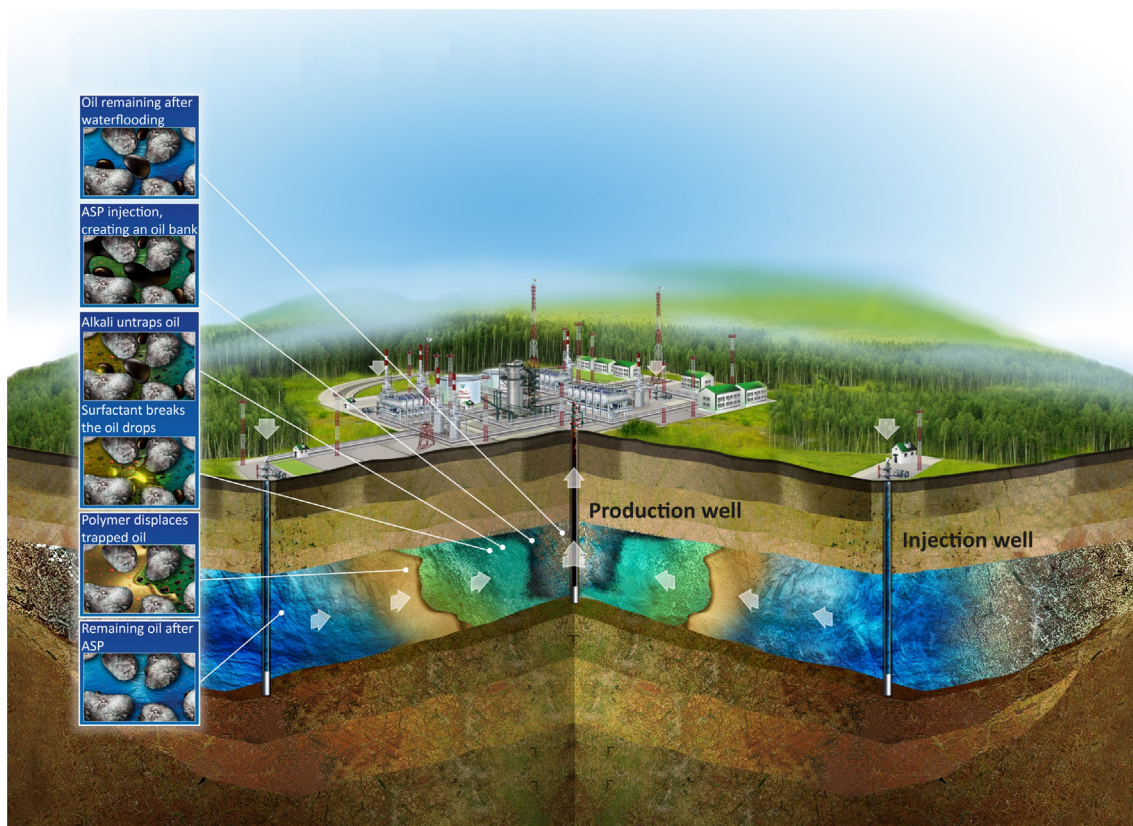
Fig. 54. Scheme of an ASP flooding describing the different stage of the recovery process with different EOR agents [459].
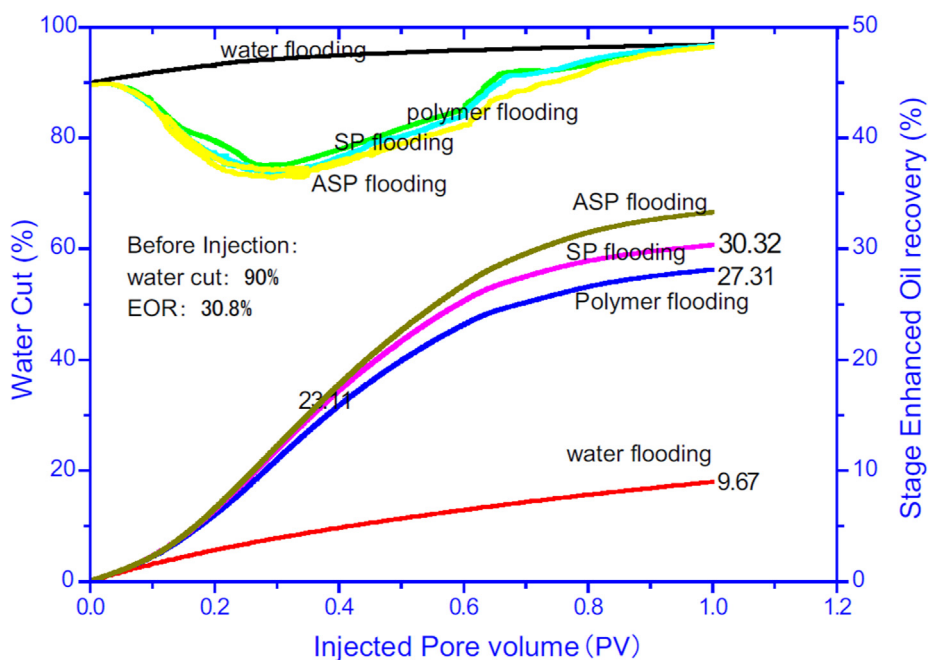
Fig. 55. The water cut and oil recovery for different EOR cases within 1 injected PV in Palouge oilfield (South Sudan) [487].

nearby the wells (Table 6). This results in excessive alkali consumption and surfactant precipitation, which was corroborated with laboratory experiments and field evaluation [455,498–500].

Sheng [63] described that a possible solution to prevent scaling, which has been carried out in Daqing, was the use of alkali-free SP flooding. Although this might solve the scale formation, the absence of alkalis increased costs in production due to reasons previously

mentioned. On the other hand, a different approach discussed is the use of scale inhibitors as a possible way to tackle this problem. Scale inhibitors are chemicals injected aimed at delaying, reducing or preventing scale formation. Most of products used work according to one of the following mechanisms:[148,501–511] prevent further grow of crystals precipitating by means of adsorbing onto their surface, or prevent the adherence of crystals precipitated to solid surfaces, such as

Fig. 56. Scheme of alkaline reactions in porous media [497].

Table 6
Alkali reactions in porous media [496].

Category	Reaction
Alkali - Water	$Ca^{2+} + 2(OH)^- \rightarrow Ca(OH)_2$
	$Mg^{2+} + 2(OH)^- \rightarrow Mg(OH)^2$
	$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
	$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$
	$Ca^{2+} + H_2SiO_4^{2-} \rightarrow CaH_2SiO_4$
Alkali - Oil	$HA_o \rightarrow HA_w$
	$HA_w \rightarrow H_3O^+ + A^-$
	$Na^+ + A^- \rightarrow NaA_w$
	$NaA_w \rightarrow NaA_o$
Alkali - Rock	Ion exchange:
	$MH + Na^+ \rightarrow MN_a + H^+$
	$M_2Ca + 2Na^+ \rightarrow 2MN_a + Ca^{2+}$
	(M denotes a mineral base exchange site)
	Congruent dissolution:
	$SiO_2(s) + 2H_2O \rightarrow Si(OH)_4$
	Incongruent dissolution:
	$CaSO_4(s) + 2NaOH \rightarrow Ca(OH)_2(s) + Na_2SO_4$

those from production facilities.

Scale inhibitors can be classified into conventional and green [510], depending on their pollution prevention features. The former are hydrophilic chemicals, mostly inorganic phosphates or organic polymers (e.g. PPCA, DETPMP, BHPMP and HDTMP) [512,513]. Green inhibitors are designed to minimize pollution by means of suppressing the use of nocive or hazardous materials [510,514–518]. According to the standards set by PARCOM (Paris Commission), a green scale inhibitor should exhibit, at least, the following characteristics: non-toxicity, biodegradability and show no bioaccumulation [519]. The phosphorus based inhibitors are being replaced by acrylate based polymers such as PAA, PAM, CMI and CATIN [515,520–526].

6.1.3. Polymer surfactant interactions

The presence of polymer and surfactant altogether modifies both the surface and rheological behavior of the solution. The most common pattern found is the creation of surfactant micelles on the polymer chain at a concentration lower than the CMC, affecting the interfacial properties (Figs. 57–59). These changes will provoke a new conformation of the polymer chain in the solution as well as the surfactant micelles may also crosslink with the polymer molecules, resulting in a gel-like structure. The result of these is the modification of solution rheological properties [483].

The interactions responsible for associations in polymer-surfactant systems are dependent on the nature of the polymer (polyeletrolyte or non-polar) and the surfactant (anionic, cationic, nonionic or zwitterionic). According to Ansari [527], these interactions are mainly of two classes: hydrophobic, between polymer-surfactant, polymer-polymer

and surfactant-surfactant (playing a major role in hydrophobically modified polymers), and electrostatic interactions between polymer-polymer, polymer-surfactant (depending on the type of charges present) and surfactant-surfactant hydrophilic heads (repulsive forces acting negatively for micellization).

As it was mentioned, one of the properties modified by this interaction is the surface tension (at a constant polymer concentration - Fig. 57). There is a first distinctive break in the surface tension curve at a concentration below the normal CMC, which is known as the Critical Aggregation Concentration (CAC or T1). This point represents the beginning of micelle formation on the polymer. As the surfactant concentration is increased, the polymer will be saturated with surfactant micelles producing a new break in the curve (T2). Thereafter the monomer surfactant concentration starts to rise again, with the direct consequence of the surface tension to decrease even more. This behavior continues up to the point when the surfactant's monomer concentration is enough to start forming free micelles (T3). Then, the surface tension curve levels, like the no-polymer curve after the CMC [360,528–531]. The conformational properties and behavior of the polymer chains are determined by, among others, the degree of ionization and the distribution and concentration of counter ions.

Taking into account Figs. 57 and 58, the next study consists in modify both concentrations (polymer and surfactant), analyzing the resultant behavior. Fig. 59 shows schematically the areas of different kind of interactions between the polymer and surfactant. Increasing the concentration of the former does not affect the CAC, but it directly modifies the amount of surfactant needed to reach points T2 (saturation) and T3 (formation of free micelles).

Fig. 57. Schematic plot of the surface tension dependence on polymer and surfactant concentration (top) and surface tension plot for a mixture of SDS (surfactant) with PVP (polymer) (bottom) [360].
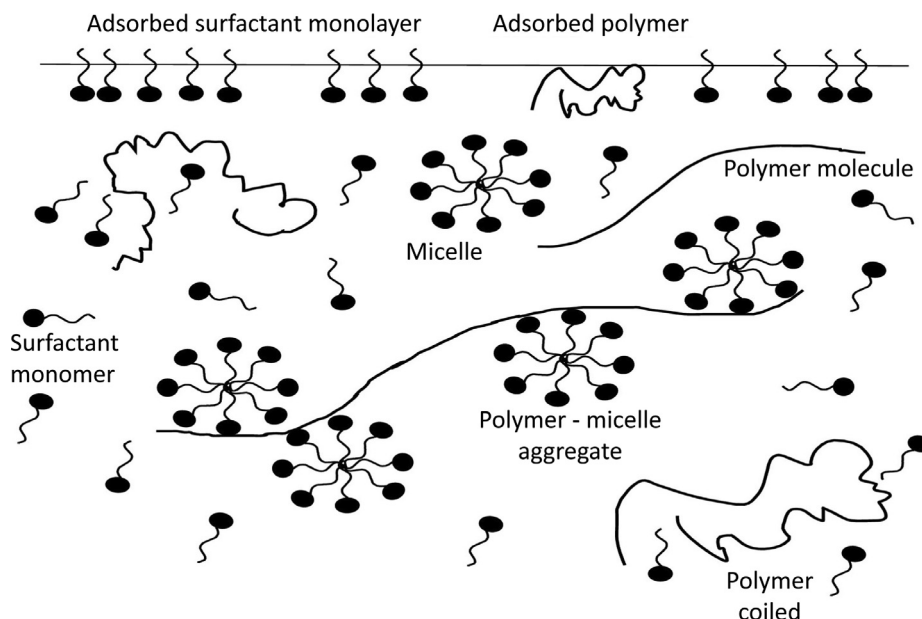
Fig. 58. Polymer-surfactant mixture and its possible interactions [532,533].
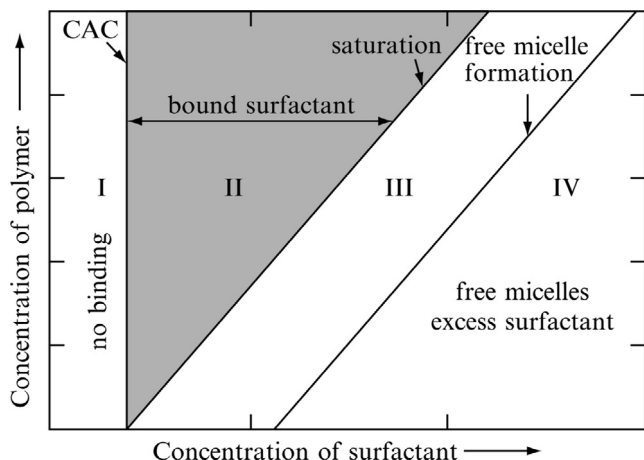

Fig. 59. Schematic plot of the different areas and interactions in a mixture surfactant polymer, as a function of concentrations [360].

For instance, Biggs [534] investigated the effects of a surfactant (SDS) in the rheological properties of a hydrophobically modified PAM. Firstly, he evaluated the viscosity of the mixture as function of the surfactant concentration, distinguishing three regions: the first region with very low surfactant concentration showed no significant increase in the viscosity; then, the second region shows a marked increase in the

viscosity which was also function of the amount of hydrophobic groups present in the polymer; and finally, the third region with the highest surfactant concentrations and viscosities similar to those from the first region and from pure polymer solution. This strong dependence on the amount of surfactant can be explained due to the nature of these associative polymers. Since the hydrophobically modified PAM contains a small amount of hydrophobic groups, this creates amphiphile polymers capable of form intra- and inter-associations (Fig. 60). This leads to enhance viscosifying properties and other rheological characteristics. The surfactant will interact with these groups, firstly strengthening the association between polymer chains, increasing the viscosity. This is a system made by the associative polymer and the surfactant micelle but, in order to have this crosslinking, there must be a significant number of hydrophobic groups per micelle. As the surfactant concentration increases, this number of groups will decrease and the crosslinking will disappear, thus decreasing the viscosity of the mixture [360].

6.1.4. Synergies in ASP flooding

Combined EOR processes make use of the properties from the chemicals being injected and this addition allows increasing the recovery efficiency. However, the synergies and interactions among these agents play a fundamental role in the recovery process as well. Thus, it is not only a "linear addition" of the benefits from each chemical agent, but also how each of these affect the each other's properties. In ASP flooding, these synergies and interactions can be summarized as follows [63].
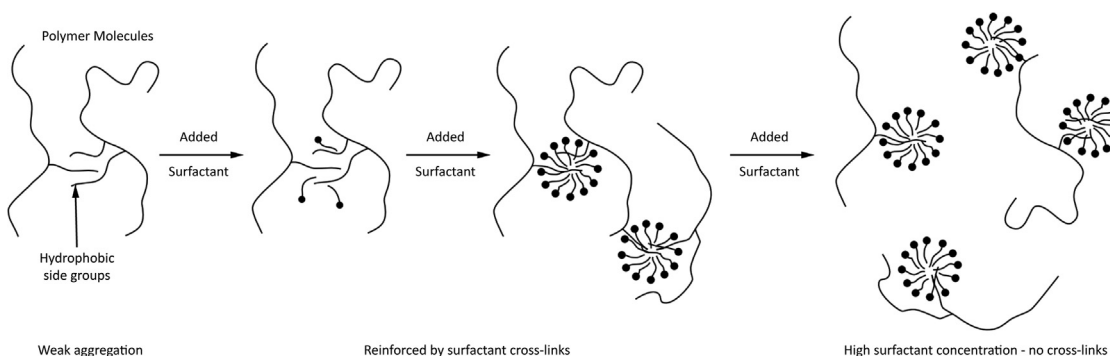

Fig. 60. Scheme of the interactions between Hydrophobically Modified PAM and a surfactant [360].

1. Alkaline injection reduces the adsorption of surfactant and polymer on the rock. Alkali is a relatively inexpensive product when compared to surfactants and polymers, so its injection and reaction with porous media provides a major economic advantage.
2. Alkali reacts with crude oil to generate soap (surfactant in situ). Soap has a low optimum salinity, whereas a synthetic surfactant has a relatively high one. The mixture of soap and the synthetic surfactant has a wider range of salinity in which the IFT is low.
3. Emulsions improve the sweep efficiency. Soap and surfactant make the former stable due to the reduced IFT. Polymer may help to stabilize emulsions since its high viscosity retard coalescence.
4. There is a competition of adsorption sites between polymer and surfactant. Therefore, adding polymer reduces surfactant adsorption, or vice versa.
5. Adding polymer improves both sweep and microscopic efficiency.

7. Conclusions

In this review a summary of the mechanisms and new trends in Chemical Enhanced Oil Recovery is presented. The need of these methods and a brief summary of its evolution have also been discussed. In the first part we have stressed the importance of developing and improving the existing energy sources while more renewable, *"green"* sources are developed. It is obvious that these cannot currently comply with the existing demands of the market, and therefore the current sources must be improved while we developed a more sustainable market.

It is evident that a huge progress has already been made on the understanding of the mechanisms in oil recovery. However, there is still a long way to reach a complete appreciation of their operation. The research on this field will lead to improve, for instance, the estimation on the factors affecting the recovery factor. It is demonstrated that a great uncertainty lies upon them, and in their assessment, early in the first stages of exploitation. The development of new techniques regarding the characterization of oilfields would help to tackle these problems, reducing the investment risk and the time required to start the exploitation.

Furthermore, a better understanding of how polymer solutions increase the microscopic efficiency using their rheological properties is considered necessary. Previous studies report that the increase in oil recovery is not only because of the enhanced rheological properties. The role of elastic stresses in viscoelastic solutions and the importance of the phenomena taking place at the water-oil interface must be analyzed as well. Also surfactants and polymeric surfactants are being under research, and it can be perceived in the literature that a better understanding of chemical synthesis processes leads to improved products. In these compounds it is essential to know how the phase behavior is in the chemical-oil-water system. This is due to the fact that the phase behavior has an impact on all parameters determining the oil recovery factor.

A review of the combined techniques in Chemical Enhanced Oil Recovery has also been presented and analyzed. The joint use of alkali, surfactants and polymers has achieved increased recovery factors with respect to standard techniques, and it is considered today as one of the most effective processes in upstream oil recovery. This is due to the synergies between the chemicals injected. In addition, the combination of these in alternate systems with gas injection presents also a great potential. However, not so much research on the topic has been published, and it is advisable further research in the chemical interactions. Also field trials should be carried out in different rock formations to determine the efficiency of combined techniques in systems with different wettabilities.

Enhanced Oil Recovery is not an exclusive field of a single discipline. The development of new chemical products and their manufacturing techniques; the best geological characterization of reservoirs and minerals that compose them; and the development of new and better materials for use in extreme and harsh conditions are just some of the areas in which new products are demanded. In these areas, an improved knowledge is required in order to overcome the current technological barriers. Furthermore, a factor that is becoming every day more important is the impact that our actions have on the environment. In several countries (e.g., Norway) there are already laws that require the use of eco-friendly and degradable products, which cannot contaminate in any way the environment after their injection. Further research on these topics must me performed in order to improve the performance of existing energy sources and processes which will be able to satisfy the future and increasing demands while newer, more sustainable energy sources are developed.

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