Enhanced Oil Recovery with Modified Nonionic Surfactants

Preparation of a Field Trial in a Sandstone Reservoir of Average Salinity

*by A. CAPELLE and W. LITTMANN**

Abstract

Practically all work on chemical flooding, both in the laboratory and in the field, has been focused on petroleum sulphonates. However, as soon as the concentration of electrolyses, especially of divalent ions, exceeds a critical value, the use of this class of anionic surfactants becomes troublesome. Some of the difficulties may be overcome by the use of additives, preferably ether sulphates or ether sulphonates. Hence, the favourable properties of nonionic substances, such as excellent stability to electrolytes, have been combined with those of anionics, and thus the so-called modified nonionics are available for chemical flooding. These products offer the possibility of chemical adaption to the reservoir conditions [1, 2], are very stable toward electrolytes, and their solubility does not depend on the temperature. The latter is a drawback of nonionic products (cloud point).

The modified nonionics are essentially anionics based on ethene oxide derivatives of alcohols or alkylphenols, with subsequent incorporation of sulphate, sulphonate, carboxyl or phosphate groups [3].

On the basis of the reservoir conditions, crude oil properties, and reservoir water, various processes have been screened for enhanced oil recovery in the Velebit reservoir. It was decided to simultaneously inject modified nonionic surfactants and polymers. In part of the reservoir, this process will be tested in two stages in a line drive with several injection wells and production wells. The total area is about 20,000 m^3. The first stage involves water flooding of about half the area, in order to collect additional data on the reservoir. During the second stage, simultaneous injection of surfactants and polymers will take place.

The reservoir is described, and possible EOR processes, the flooding concept and selection of chemicals are discussed.

Reservoir description

The reservoir has the form of a semicircle and is bordered by a fault in the NE direction. It is capped by a clay layer (Pliocene) and underlain by clay containing water-saturated sand. The northeastern part dips steeply (figure 1).

The planned pilot test area is located in the SW part (figure 2). There exists a marked anticlinal structure, with top at 739 m below the surface, 633.5 m below sea level. The reservoir itself is subdivided into two layers, pay zone 2 and the underlying pay zone 1 (figure 3).

Pay zone 2 consists of highly porous sand with porosity about 30 per cent. The grain size distribution varies between 20 and 200 µm. The clay content is about 1 per cent; at some locations the carbonate content is rather high, with as much as 35 per cent. The average thickness is 12.5 m.

Pay zone 1 is also very porous. The grain size distribution ranges from 100 to 500 µm, locally up to 200 µm. The clay content is higher and shows a greater variation (5 to 15 per cent), whereas that of carbonate is lower (5 to 15 per cent). The average thickness is 17 m.

The grain size distribution and core analysis indicate that the permeability varies between 0.2 and 6 µm^2.

The reservoir temperature exhibits a gradient from 63 to 73° C, due to the infiltration of hot water from lower strata. The salinity of the reservoir water is 12 kg/m^3 for pay zone 2 and 10 kg/m^3 for pay zone 1, with a Ca^{++} concentration of 80 g/m^3. The density of the oil is 917 kg/m^3 at 20° C, and its viscosity is 7.5 mPa · s under reservoir conditions. The production mechanism are water drive and gas cap drive. The oil-water contact is located at 667 m and the gas-oil contact at 636 m below sea level.

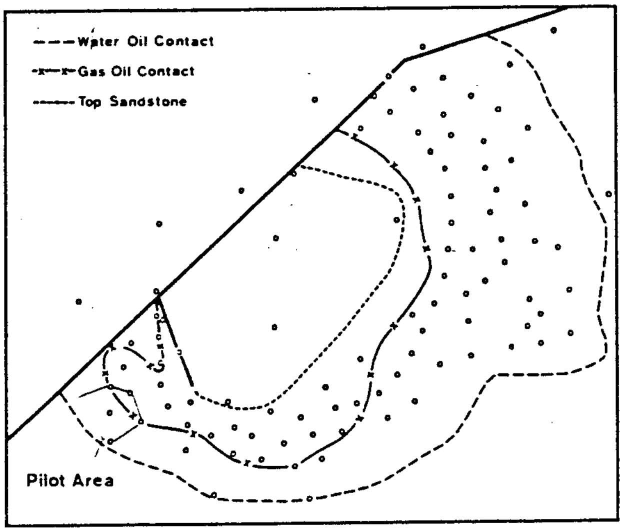

Fig. 1: Velebit oil field – structure map

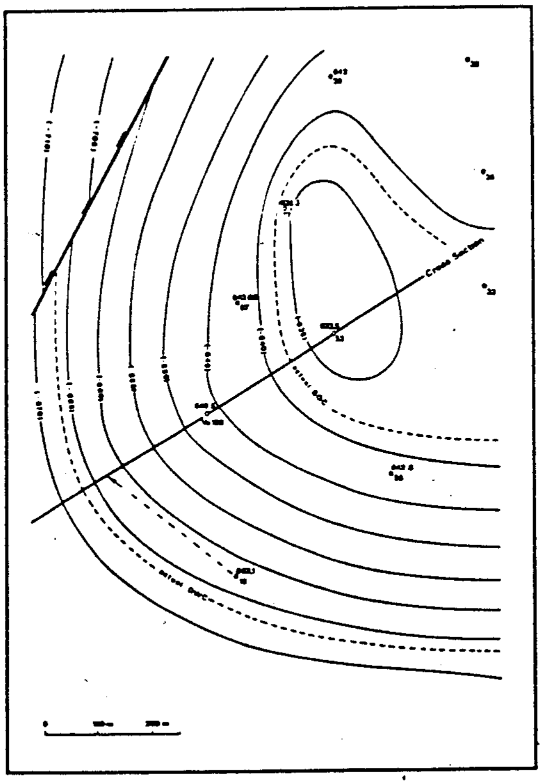

Fig. 2: Velebit oil field – top Pliozene/pay zone 2 (structure map)

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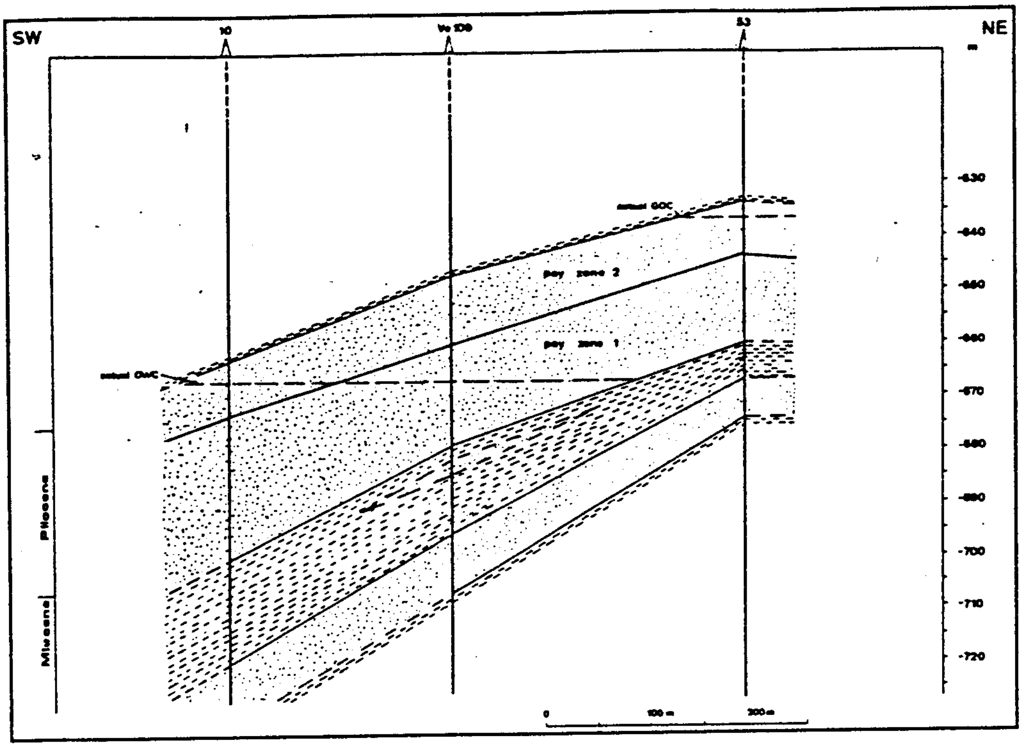

Fig. 3: Velebit oil field – cross section (SW-NE) (log correlation)

Production history

The oil field was put into production in 1968, and 82 wells have been drilled since then.
The oil in place is estimated at $25 \cdot 10^6$ m^3. The cumulative oil production prior 1980 was $3.6 \cdot 10^6$ m^3, which corresponds to a recovery of 14.5 per cent. At an average GOR of 26 m^3/m^3, the cumulative gas production is $94 \cdot 10^6$ m^3.
The water cut remained below 3 per cent until 1975, and subsequently increased to a value of 8 per cent.
The reservoir pressure has declined by only 2 bar from an initial value of 75 bar since the start of production. This can be explained by the presence of an active edge water drive. The major production mechanism is water drive.
Prior to 1972 oil production increased continuously, and an average production of 260,000 m^3/a was expected. Through the drilling of additional wells since 1974, the production was augmented to 400,000 m^3/a. The peak production has not yet been reached, but oil production is levelling off at about 400,000 m^3/a with a steep increase in water cut. In order to maintain this level in the future, the application of EOR methods must now be considered.

Possible EOR processes

Despite the large variation and high value of the carbonate content in this reservoir, the use of chemicals for enhancing the oil recovery appears promising.
Polymer or surfactant flooding, or a combination of both, are possible approaches. The reservoir data are compiled in table 1. Because of the low viscosity of the crude oil under reservoir conditions, the cost of polymer flooding is not expected to be high. The use of partially hydrolysed polyacrylamides or polysaccharides is feasible; the salinity may be a problem for polyacrylamides. The high permeability excludes injectivity problems.
The salinity of the reservoir water (table 2) and the temperature are ideally suited for the application of surfactants, especially the modified nonionics, which offer the possibility of chemical tailoring to suit the reservoir conditions. To increase the sweep efficiency of a surfactant solution in this highly permeable reservoir, a simultaneous injection of the surfactant and polymer is suggested. Of course, the latter requires an intensive study of the polymer-surfactant interaction.

Flooding concept

The limiting factors for any flooding concept are the active edge water drive and the gas cap. It is imperative to avoid disturbing the gas cap. To prevent loss of chemicals into the aquifer, such measures as "back pressure wells" or the injection of blocking agents have to be taken.

Table 1 Reservoir Brine Analysis Velebit

$NaCl$	6370 g/m^3
$NaHCO_3$	3700 g/m^3
Na_2CO_3	110 g/m^3
$Na_2SO_4\ 10\ H_2O$	230 g/m^3
KCl	220 g/m^3
$CaCl_2 \cdot 2\ H_2O$	80 g/m^3
$SrCl_2 \cdot 6\ H_2O$	10 g/m^3
$BaCl_2 \cdot 2\ H_2O$	20 g/m^3
$MgCl_2 \cdot 6\ H_2O$	120 g/m^3
NH_4Cl	90 g/m^3

Table 2 Reservoir Data Velebit

Formation Thickness	35 m
Porosity	30 %
Permeability	0.3–6 µm^2
Oil Viscosity (under reservoir cond.)	7.5 m Pa · s
Oil Density (at 20° C)	917 kg/m^3
Formation Temperature	63–73° C
Sand (Modes of Grain Size Distribution)	0.1–2 mm
Clay Content	1 %
Carbonate Content	5–40 %
Salinity of Brine	10–12 kg/m^3

The following procedure is suggested:
Flooding should be commenced to produce the oil in the area between wells Ve 10 and Ve 9 in a line drive. For this purpose two additional wells are to be drilled in line with well Ve 10 and parallel to the edge water. Water injection will be applied because of the relatively low oil saturation in this part of the reservoir, as a result of the high water table, and in order to study the flood performance and to adjust the reservoir simulation.
After completion of the water flood, the injection wells in line with Ve 10 will be utilized as back pressure wells, and the other two wells in line with Ve 109 will serve as injection wells for the chemical solutions (figure 4). The back pressure wells will be employed for supporting the water

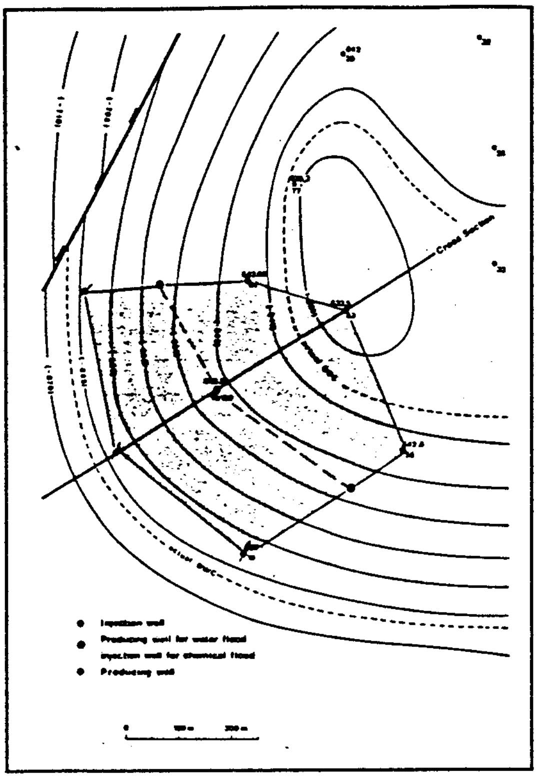

Fig. 4: Velebit oil field – top Pliozene/pay zone 2 (structure map)

drive of the aquifer and thus reduce the loss of chemicals into areas where no additional oil may be recovered. The flooding concept involves a line drive in two stages. It starts with a water flood from the aquifer, and continues with chemical flooding in the second line, with the use of the injection wells of the water flood as back pressure wells for combined surfactant-polymer flooding (figure 5).

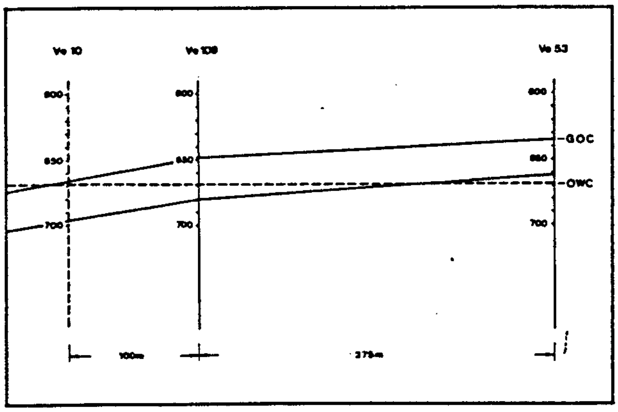

Fig. 5: Velebit reservoir – cross section

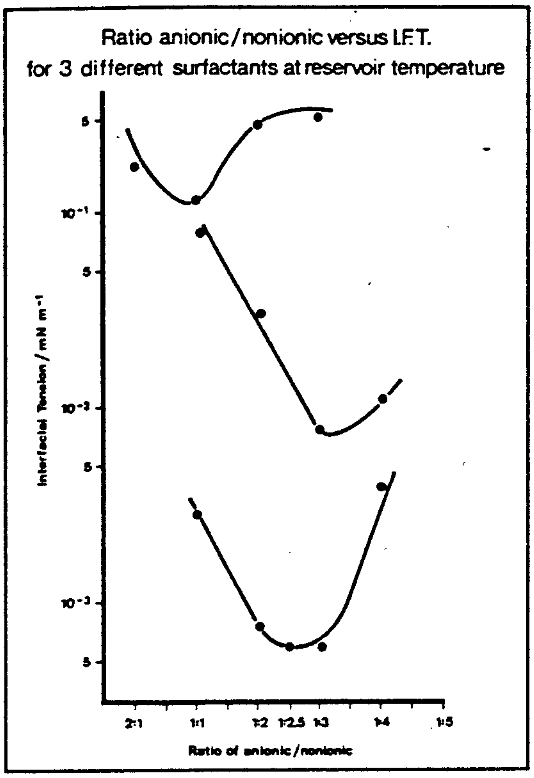

Fig. 6: Ratio anionic/ionic versus I. F. T. for three different surfactants at reservoir temperature

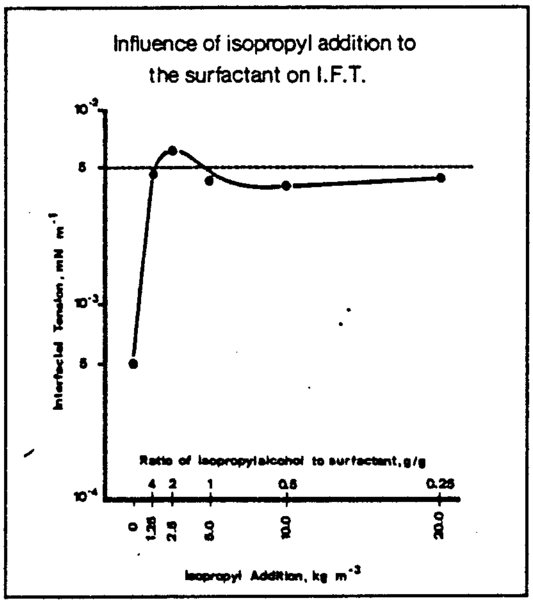

Fig. 7: Influence of isopropyl alcohol addition to the surfactant on I. F. T.

Choice of chemicals

Surfactants

Surfactants are used to overcome the capillary forces which trap the crude oil in the reservoir. The interfacial tension between the aqueous and oil phases provides a measure of these forces. Crude oil can be mobilized from the reservoir if the interfacial tension can be decreased to a value less than 10^{-3} mN/m.

The main objective is to investigate the parameters which influence the interfacial tension. Modified nonionics were thereby used. These substances comprise both ethene oxide and anionic groups, which allow modification for optimal adaptation to the reservoir conditions [1, 2]. The general formula is given in table 3.

Original crude oil and water from the Velebit field, together with original reservoir rock, were used for all investigations. The crude oil was dehydrated by heating and subsequent centrifugation at 1600 min^{-1} and 20° C. The residual water content of the crude oil was determined analytically by the Karl Fischer titration and was found to be 0.04 per cent.

Thermostability

The thermostability of the optimal surfactant was investigated under reservoir conditions. Original crude oil and forma-

Table 3 Chemical Formula of Modified Nonionic Surfactants

$R - (OCH_2CH_2)_N - O - X$

or

$R - (OCH_2CH_2)_N - X$

R	N	X
Variable	Variable	Variable Con. Variable

With R: Hydrophobic Rest Like Alcohols or Alkylphenols
N: Number of Alkyleneoxide Groups
X: Anionic Group such as Sulfate
Sulfonate
Phosphate
Phosphonate
Carboxylate

tion water were thereby used. Ground reservoir rock was taken as representative.

The following was sealed into high pressure glass tubes (2.00 cm OD, 28 cm in lenght) under liquid nitrogen:

13.6 g reservoir water with 5 per cent dissolved surfactant,
25.0 g ground reservoir rock, and
11.4 g crude oil.

The filled vessels are then placed in a test cabinet at 63° C and rotated perpendicularly to their axes at 30 min^{-1}. The samples were titrated (Hellsten method) to determine the concentrations of the components at different times (table 4). It can safely be concluded that no degradation of the chemicals will occur in the reservoir for the duration of the test (1a).

Table 4 Thermostability
Analytical Determination of Active Content

Theoretical	Observed
0.022	Exposure 3 weeks 0.022 6 weeks 0.021 9 weeks 0.022 10 weeks 0.021 40 weeks 0.021

Interfacial tension

The interfacial tension between crude oil and surfactant solutions was measured by using a spinning drop interfacial tensiometer according to Wade. The rotational speed of the glass capillary (2.00 mm ID) was varied between 4000 and 9600 min^{-1}; the final measurements were carried out at 7000 min^{-1}. The temperature was varied between 25 and 75° C. The concentration of the surfactants varied between 100 g/m^3 and 100 kg/m^3. The influence of alcohol was studied too. The interfacial tension was calculated by means of the Vonnegut approximation:

$$\gamma = \frac{\Delta\varrho\omega}{4C}$$

whereby γ denotes the interfacial tension,
$\Delta\varrho$ denotes the density difference,
ω denotes the angular velocity, and
C is a tabulated value.

The crude oil and surfactant solution were mutually equilibrated prior to each measurement.

With respect to temperature (50 to 65° C) (figure 8) and concentration (2 to 30 kg/m^3) (figure 9), the surfactant exhibits a certain range of applicability, in which the interfacial tension remains below the value of 10^{-3} mN/m. Its location can be shifted by the addition of isopropyl alcohol. This is important, because a slight decrease of the formation temperature occurs during injection, and the surfactant concentration may alter during flooding. Moreover, a temperature gradient can develop because of infiltration of hot water from underlying strata.

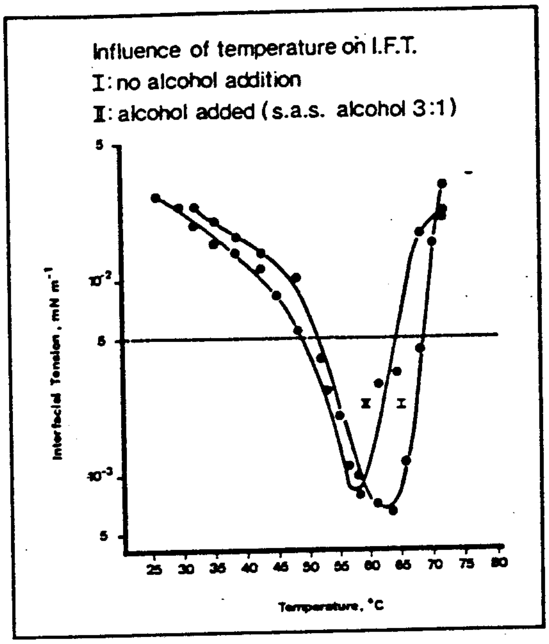

Fig. 8: Influence of temperature on I. F. T.
I. no alcohol addition
II. alcohol added (s. a. s. alcohol 3:1)

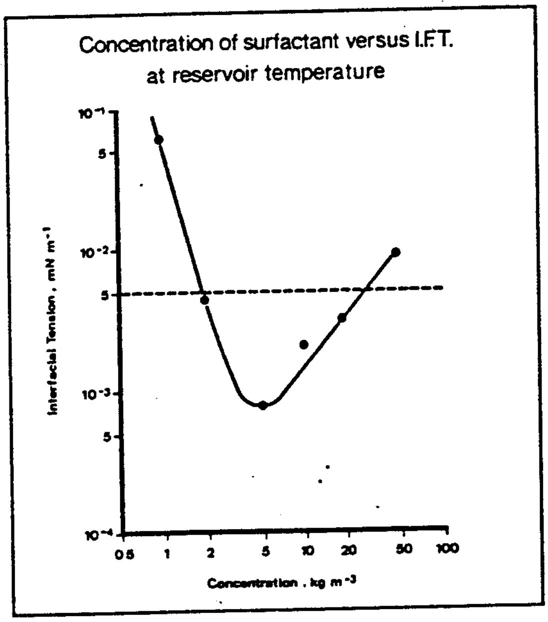

Fig. 9: Concentration of surfactant versus I. F. T. at reservoir temperature

Adsorption

The loss of surfactant due to adsorption is a very important characteristic, since a minimal concentration must be maintained during the entire process.

The adsorption was measured on 10 g of ground reservoir rock immersed in 150 cm^3 of reservoir water with dissolved surfactant. The ground rock is classified according to sieve analysis. It has a specific surface area of 2100 cm^2/g. The surfactant concentration varies between 5 g/m^3 and 50 kg/m^3. The vessels are shaken for 16 h in order to obtain maximal adsorption at room temperature. The fluid is then separated by centrifugation, and the surfactant concentration is determined analytically. The amount adsorbed, calculated from the difference between the initial and final concentrations, is plotted in mg/g.

For the concentration suggested for application, the irreversible adsorption of the surfactant is very slight ($< 10^{-3}$ g/g). The addition of polymer to the surfactant solution suppresses the adsorption even further ($< 10^{-4}$ g/g). With residual reservoir water and oil present in the adsorbent, the adsorption is also very slight. Although the data are limited by the accuracy of the analytical method applied, they indicate $< 10^{-4}$ g/g.

Compatibility with reservoir brine

Compatibility of the chemicals used with the reservoir fluids is vital for avoiding plugging of the porous medium. Although this danger is almost negligible because of the high permeability, the small capillaries where most of the oil is trapped are critical. Solutions of surfactant in reservoir water were observed visually for the occurrence of precipitates or of a haze. At all concentrations, the proposed surfactant did not form a precipitate or haze, either alone or in combination with the proposed polymer (table 5).

Table 5 Compatability of Chemicals with Reservoir Brine

Concentration	Petroleum Sulfonate	Modified Nonionic Surfactants (MNIS)	Polyacrylamide (PAA)	Polysaccaride (PS)	MNIS + 500 g/m³ PAA	MNIS + 500 g/m³ PS
50 g/m³	+++	+++				
100 g/m³	++	+++				
500 g/m³	±	++	±	±		
1 kg/m³	±	++				
5 kg/m³	−−	±				
10 kg/m³	−−	±			±	±
50 kg/m³	−−−	±				

+++ Clear soluble ± Haze −− Slight precipitation
++ Slight haze −−− Precipitation

Polymers

Commercially available polymers, partially hydrolysed polyacrylamides and polysaccharides, were investigated. Attention was focused on interactions in aqueous solutions; precipitation and incompatibility were studied visually at reservoir temperature. The viscosity was measured as a function of the temperature and shear rate.

Compatibility with surfactant and reservoir brine

Equal volumes of surfactant solution (concentration 5 kg/m³) and polymer solution (0.5 kg/m³) were mixed and thermostated at different temperatures (−5, 4, 20, and 63° C) for 24 h. The results of visual observations are compiled in table 5.

A stock solution of the polymers was prepared by dissolving them in well-defined fresh water (surface water) at a concentration of 5 kg/m³. This solution was subsequently diluted in synthetic reservoir brine containing the surfactant at a concentration of 5 kg/m³.

Most types of partially hydrolysed polyacrylamides showed precipitation or phase separation in combination with the surfactant in reservoir water. A polysaccharide and a partially hydrolysed polyacrylamide which exhibited good compatibility were used for further studies.

Viscosity measurements

The viscosity of different polymer and polymer-surfactant solutions in reservoir brine was investigated at different temperatures (20 and 63° C) and different shear rates (0.4 to 70 s^{-1}, at 0.3 to 60 min^{-1}), with a Brookfield LVT viscosimeter. Hardly any influence was exerted by the surfactant on the polymers with good compatibility. A certain synergistic effect may be deduced from the results. Flow curves for the polymers in fresh water, in reservoir brine, and together with the surfactant, at 20 and 63° C, are plotted in figures 10 and 11.

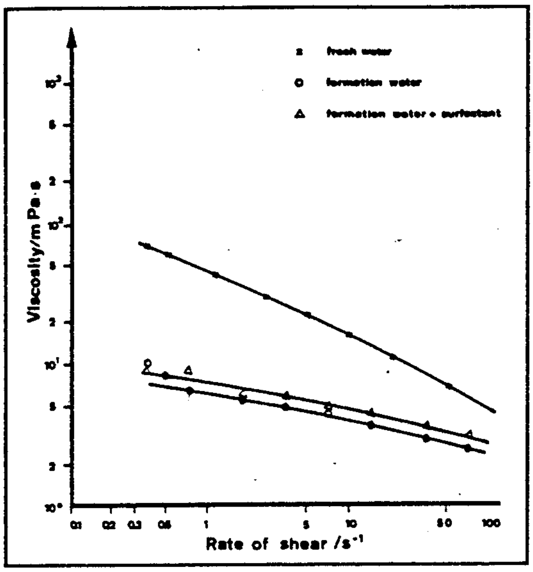

Fig. 10: Flow curves for polyacrylamide 460 ppm, 63° C

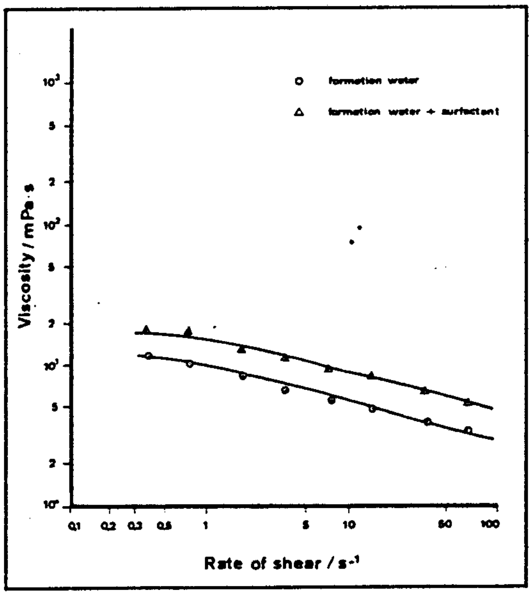

Fig. 11: Flow curves for xanthane gum 600 ppm, 63° C

Injectivity

The polymer-surfactant solutions were screened for their injectivity by flooding in sand packs. The permeability was in the same range as in the reservoir. The pressure gradient was recorded as a function of the injected volume.

References

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