

## Application of Modified Non-Ionic Surface Active Agents in Enhanced Oil Recovery

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### ABSTRACT

As early as 1954 a study into the efficiency of nonionic detergents to displace crude oil from sandstone reservoirs was published by Dunning. In this study different oxyethylated alkylphenols were investigated and it was concluded that this class of surfactants was among the most promising, provided the solubility in the injected waters at reservoir temperatures is sufficient. Since then hardly any investigation into these chemicals were carried out. Practically all work on chemical flooding, both in the laboratory and in the field has been focussed on petroleum sulfonates. Why this investigation into modified nonionics? The main reason is the excellent stability against electrolytes, a feature petroleum sulfonates do not have.

By combining the favourable properties of both the nonionics and anionics the so called modified nonionics were introduced for chemical flooding. The products show an excellent stability against electrolytes, especially divalent ions, and no temperature dependence of their solubility.

Illustrated by a practical example: sandstone reservoir, average salinity and medium temperature, the development of a flooding recipe based on modified nonionics will be discussed.

Attention will be focussed on the laboratory investigation and the optimization of the flooding recipe. It has been shown that a 50% pv slug containing about 0.5% surfactant will give about 35% incremental oil.

### INTRODUCTION

As early as 1954 a study into the efficiency of nonionic surfactants to displace crude oil from sandstone reservoirs was published by Dunning (1). In this study different oxyethylated alkylphenols were investigated and it was concluded that this class of surfactants was among the most promising, providing the solubility in the injected water under surface and reservoir conditions is sufficient. For

References and illustrations at end of paper.

a maximum displacement efficiency the mole ratio of ethylene oxide varied between 4 and 12, dependent on crude oil, reservoir water and reservoir conditions. This result was confirmed by Wade et al (2), who applying the EACN concept found minimum interfacial tension between crude oil and solutions of oxyethylated alkylphenols and alcohols in reservoir water at a mole ratio between 3.5 and 12.

Gogarty (3) gives an extensive overview of the research in chemical flooding over the last years. Several types of chemicals are discussed but attention is focussed on petroleum sulfonates. Petroleum sulfonates have been tested since about 1960 in fieldtrials, demonstration projects etc. showing their potential to increase the recovery factor.

Petroleum sulfonates are limited in their application. With increasing salinity of the reservoir water, especially the divalent ( $\text{Ca}^{++}$ ) ions the solubility decreases. When a critical value in salinity and divalent ions is reached, this value is roughly 1% salinity, 100 ppm  $\text{Ca}^{++}$ , petroleum sulfonates precipitate leading to possible plugging (Table 1). Several methods have been proposed and tried out to overcome this problem, f.i. preflushing of a highly saline reservoir with sweet water, addition of other chemicals to the petroleum sulfonate solution, tailoring the petroleum sulfonate with respect to its equivalent weight. The salinity gradient concept is an illustration of this (4).

Nonionic surfactants are reaction products of an alkylene oxide f.i. ethylene oxide, and molecules containing an acidic H-atom like alcohols or alkylphenols. Nonionic surfactants contain hydrophobic and hydrophilic parts, the ratio is expressed as the Hydrophilic-Lipophilic Balance (5). When a nonionic surfactant dissolved in water is heated phase separation, observed as a haze, will occur at a certain temperature. This temperature is called the cloudpoint. Below the cloudpoint the ethylene oxide groups of the molecule are hydrated and hence the molecule is soluble in water. Above the cloudpoint the water molecules are split off and phase separation occurs. Addition of electrolytes to the non-ionic surfactant solution decreases the cloudpoint.

As long as the cloudpoint is not reached the solubility of the nonionic surfactant is excellent in all kinds of electrolyte containing water.

By combining the properties of the nonionics with petroleum sulfonates, chemically and not as a mixture, the so called modified nonionic surfactants (table 2) were introduced into the application for enhanced oil recovery. Of course we should realize we are still dealing with anionic surfactants. The chemical and physical properties are those of anionics.

The conversion of the nonionic molecule to an anionic molecule can be varied by adjusting the process variables, resulting in principle in mixtures of nonionic and anionic compounds. All these variables make it possible to adapt chemically the surfactant molecule to the reservoir conditions, rather than the opposite as is the case with petroleum sulfonates (6).

The effect of some of the variables on physical properties important for e.o.r. application has been reported by Balzer (7) who studied the influence of the number of ethylene oxide groups and the conversion factor on the Phase Inversion Temperature (PIT) for carboxylates. With increasing ethylene oxide content and increasing conversion the PIT increases for a given carboxylate in a given reservoir system. In this paper the influence of the number of ethylene oxide groups and conversion factor for sulfates on I.F.T. and adsorption is presented. With increasing number of ethylene oxide groups the I.F.T. increases, the adsorption decreases (fig. 1, 2) The influence of the conversion factor is more complex (fig. 3). The I.F.T. decreases with the conversion factor till a minimum is reached, after which a increase is observed.

For a sandstone reservoir of average salinity and medium temperature a flooding recipe based on modified nonionic surfactants has been developed. This recipe will be applied in a fieldtrial in part of this reservoir.

#### Reservoir description

The reservoir (Velebit oilfield, Yugoslavia) extends as a half circle, bordered by a fault in N.E. direction. It is capped by a clay layer (pliocene) and underlain by clay containing water saturated sands. The N.E. part is steeply dipping. (fig. 4).

The pilot area is in the S.W. part of the field. There exists an anticlinal structure, top at 739 below surface, 633.5 m sub sea level. The reservoir is divided into two layers, payzone 1 and payzone 2. (fig. 5, 6).

Payzone 2 consists of a very porous sand with porosity about 30%. The modes of the grain size distribution of the sands range between 20 - 200  $\mu\text{m}$ . Clay content is about 1%. In some places there is rather high carbonate content up to 35%. Average thickness 12.5 m.

Payzone 1 is also very porous, the same as payzone 2, the modes of the grain size distribution of the sand, range from 100 - 500  $\mu\text{m}$ , in some places up to 2000  $\mu\text{m}$ . Clay content is higher and shows a greater variation (5% - 15%), the carbonate content is lower, between 5%-15%. Average thickness 17 m.

Based on grain size distribution and core analysis the permeability varies between 0.2 - 6  $\mu\text{m}^2$ .

The reservoir temperature shows a gradient from 63°C - 73°C, due to the infiltration of hot water. The salinity of the reservoir water is for payzone 2: 12 kg/m<sup>3</sup> and payzone 1: 10 kg/m<sup>3</sup> with a Ca<sup>++</sup> content of 80 g/m<sup>3</sup>. (Table 4) Oil density is 917 kg/m<sup>3</sup> at 20°C. Oil viscosity under reservoir conditions 7.5 mPa.s. (Table 3) The production mechanisms are water drive and gascap drive. Oil-water contact is at 667 m below sea level and gas-oil contact at 663 m below sea level.

#### Production history

The oilfield was taken into production in 1968 and since then 82 wells have been drilled.

The OIP is estimated at 25.10<sup>6</sup> m<sup>3</sup> (160.10<sup>6</sup> bbl)<sub>3</sub>, The cumulative oil production till 1980 is 3.6 10<sup>6</sup> m<sup>3</sup>, which equals a<sub>3</sub> recovery of 14.5%. At an average GOR of 26 m<sup>3</sup>/m<sup>3</sup> the cumulative gas production is 94.10 m<sup>3</sup>

The reservoir pressure declined about 2 bars since the start of production from the initial value of 75 bars. The oil water contact rose about 90 cm. There is an active edge water drive, the major natural production mechanism.

Oil production increased continuously till 1972 and an average yearly production of 260.000 m<sup>3</sup> was expected. By drilling additional wells since 1974 the production could be increased to 400.000 m<sup>3</sup>/year. The peak production is still not reached, but oil production is levelling off at about 400.000 m<sup>3</sup> with a steep increase in water cut.

To maintain production at the same level in the forthcoming years EOR methods are discussed.

#### Possible E.O.R. processes

As flooding processes, polymer flooding, surfactant flooding or a combination of both are possibilities. Due to the low viscosity of the crude oil under reservoir conditions the expected cost for polymer flooding will be low. Both partially hydrolysed polyacrylamides and polysaccharides could be used, the salinity may be a problem for polyacrylamides. The high permeabilities exclude injectivity problems.

To increase the sweep efficiency of a surfactant solution in this high permeable reservoir a simultaneous injection of the surfactant and polymer is suggested. Of course the latter leads to an intensive study of polymer surfactant interaction.

#### Flooding concept

The limiting factors for any flooding concept to be discussed are:

Active edge water drive and the gascap. It is imperative to avoid all kind of troubles that the gascap is not disturbed. To prevent loss of chemicals in the aquifer measures like "backpressure wells" or injection of blocking agents have to be taken.

The following procedure is suggested:

Flooding should be commenced to produce the oil in the area between wells Ve 10 and Ve 109 in a line drive. For this purpose two additional wells will be drilled in a line with well Ve 10 parallel to the edge water. This area will be flooded by water injection for several reasons:

one is the relatively low oil saturation in this part of the reservoir, because of the high water table, another is 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 used as backpressure wells, and two other wells in line with Ve 109 will be used as injection wells for the chemical solutions. The backpressure wells will be used to support the water drive of the aquifer and thus reduce the loss of chemicals into areas, where no additional oil can be recovered. This flooding concept is a line drive in two stages. It will start with a water flood from the aquifer and continue with chemical flooding in the second line, using the injection wells of the water flood as back pressure wells for the combined surfactant/polymer flood. (Fig. 5) The specifics will be reported later after finalizing a reservoir simulation.

#### Choice of the chemicals

##### A. Surfactants.

Following investigations were carried out:

- interfacial tension measurement
- adsorption studies
- compatibility
- thermostability

##### Interfacial Tension

Interfacial tension measurement between crude oil and surfactant solutions in reservoir water were carried out using a spinning drop interfacial tensiometer (8). The influence of isopropyl alcohol was also studied. The results are shown in figs. 7 to 9.

As can be seen from the results there is a certain application window for the surfactant, in which the interfacial tension always remains below the value of  $10^{-3}$  mN/m. This window exists with respect to temperature (50-65°C) (fig. 7) and can be shifted by addition of isopropyl alcohol (fig. 8) and with respect to concentration (fig. 9) (between 2-30 kg/m<sup>3</sup>). This is important because during injection a slight decrease of the formation temperature will occur and subsequent flooding will dilute the surfactant.

Due to infiltration of hot water from underlying layer a temperature gradient can develop.

##### Adsorption

Adsorption losses were measured statically and

dynamically. At a concentration of 50 kg/m<sup>3</sup> the irreversible adsorption is very low. ( $<10^{-3}$  g/g).

The addition of polymer to the surfactant solution decreases the adsorption even further ( $<10^{-4}$  g/g). With residual reservoir water and oil present in the adsorbent the adsorption is also very small. Data are limited by the accuracy of the analytical method used, at least they are  $<10^{-4}$  4).

##### Compatibility

Compatibility of the used chemicals with the reservoir fluids is very important to avoid plugging of the reservoir.

Solutions of surfactant in reservoir water were observed visually for precipitates or occurrence of a haze. In all concentrations, neither the proposed surfactant shows precipitation nor in combination with the proposed polymer.

##### Thermostability

The thermostability of the modified nonionic surfactant was investigated under reservoir condition. Surfactant solution in reservoir water, grounded reservoir rock and crude oil was put in high pressure glass bombs. After different exposure times the contents were checked analytically (table 5). No degradation of the chemical was found.

##### B. Polymers

Commercially available polymers, partially hydrolyzed polyacrylamides and polysaccharides were investigated. Attention was focussed on interaction studies in aqueous solutions. Precipitation, incompatibility were studied visually in aqueous solutions at reservoir temperature. Viscosity studies were done as function of temperature and rate of shear.

##### Compatibility

Equal volumes of surfactant solutions (concentration 5 kg/m<sup>3</sup>) and polymer solutions, conc. 0.5 kg/m<sup>3</sup> were mixed together. The solutions were thermostatted at different temperatures (-5°C, 4°C, 20°C and 63°C) for 24 hours. After this the solutions were visually observed.

A stock solution of the polymers was prepared by mixing the polymers in a well defined fresh water (surface water) at a concentration of 5 kg/m<sup>3</sup>. This solution was diluted in a reservoir brine containing the surfactant at a concentration of 5 kg/m<sup>3</sup>.

##### Results

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

##### Viscosity measurement

The viscosity of different polymer solutions in reservoir water and of different polymer surfactant solutions was investigated with a Brookfield

UVI viscosimeter with 17 adaptor. Investigations were carried out at different temperatures (-5°C, 2°C, 20°C and 63°C) and different rates of shear, ranging from 0.4 to 70 sec<sup>-1</sup> (0.3 rpm to 60 rpm with spindle diameter 2.5 cm and measuring vessel 2.7 cm. Hardly any influence of the surfactant on the polymers with good compatibility could be found. A certain synergistic effect maybe deduced from the results (figs. 10, 11).

#### Injectivity

The injectivity of the polymer-surfactant solutions was screened by flooding sandpacks. The permeability was in the same range as the reservoir. As a function of injected volume the pressure gradient was recorded.

#### Flooding Tests

Flooding tests were carried out in a laboratory flooding apparatus with sandpacks. The permeability and porosity of the sandpack was kept identical with those of the reservoir. A 50% pv slug containing 0.5% modified nonionic surfactant with 0.05% polymer results in about 35% incremental oil (fig. 12).

#### Acknowledgment

We thank Dr. W. Littmann of Veba Oel AG for the work on the reservoir description.

#### References

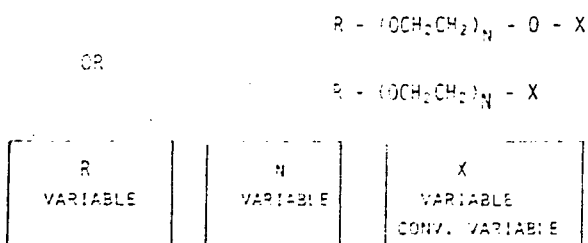
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TABLE 1: SOLUBILITY IN RESERVOIR WATER

CON.	PETR. SULF.	MNIS	P.A.A.	P.S.	MNIS + 500g/m <sup>3</sup> P.A.A.	MNIS + 500 g/m <sup>3</sup> P.S.
50 g/m <sup>3</sup>	+++	+++				
100 g/m <sup>3</sup>	++	+++				
500 g/m <sup>3</sup>	±	++	±	±		
1 kg/m <sup>3</sup>	±	++				
5 kg/m <sup>3</sup>	--	±				
10 kg/m <sup>3</sup>	--	±			±	±
50 kg/m <sup>3</sup>	---	±				

- +++ CLEAR SOLUBLE
- ++ SLIGHT HAZE
- ± HAZE
- SLIGHT PRECIPITATION
- PRECIPITATION

TABLE 2: CHEMICAL FORMULA OF MODIFIED  
NON IONIC SURFACTANTS



WITH R : HYDROPHOBIC REST LIKE ALCOHOLS OR ALKYLPHENOLS

N : NUMBER OF ALKYLENEOXIDE GROUPS

X : ANIONIC GROUP SUCH AS SULFATE

SULFONATE

PHOSPHATE

PHOSPHONATE

CARBOXYLATE

Table 3: Reservoir Data Velebit

Formation Thickness	35 m
Porosity	30 %
Permeability	03-6 $\mu\text{m}^2$
Oil Viscosity (under reservoir cond.)	7.5 m Pa .s
Oil Density (at 20°C)	917 kg/m <sup>3</sup>
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 <sup>3</sup>

Table 4: Reservoir Brine Analysis Velebit

Na Cl	6370	g /m <sup>3</sup>
Na HCO <sub>3</sub>	700	
Na <sub>2</sub> CO <sub>3</sub>	110	
Na <sub>2</sub> SO <sub>4</sub> 10 H <sub>2</sub> O	230	
K Cl	220	
Ca Cl <sub>2</sub> · 2H <sub>2</sub> O	80	
Sr Cl <sub>2</sub> · 6H <sub>2</sub> O	10	
Ba Cl <sub>2</sub> · 2H <sub>2</sub> O	20	
Mg Cl <sub>2</sub> · 6H <sub>2</sub> O	120	
NH <sub>4</sub> Cl	90	

TABLE 5: THERMOSTABILITY

ANALYTICAL DETERMINATION OF ACTIVE CONTENT

THEORETICALLY	OBSERVED
0.022	EXPOSURE 3 WEEKS 0.022 6 WEEKS 0.021 9 WEEKS 0.022 10 WEEKS 0.021 40 WEEKS 0.021

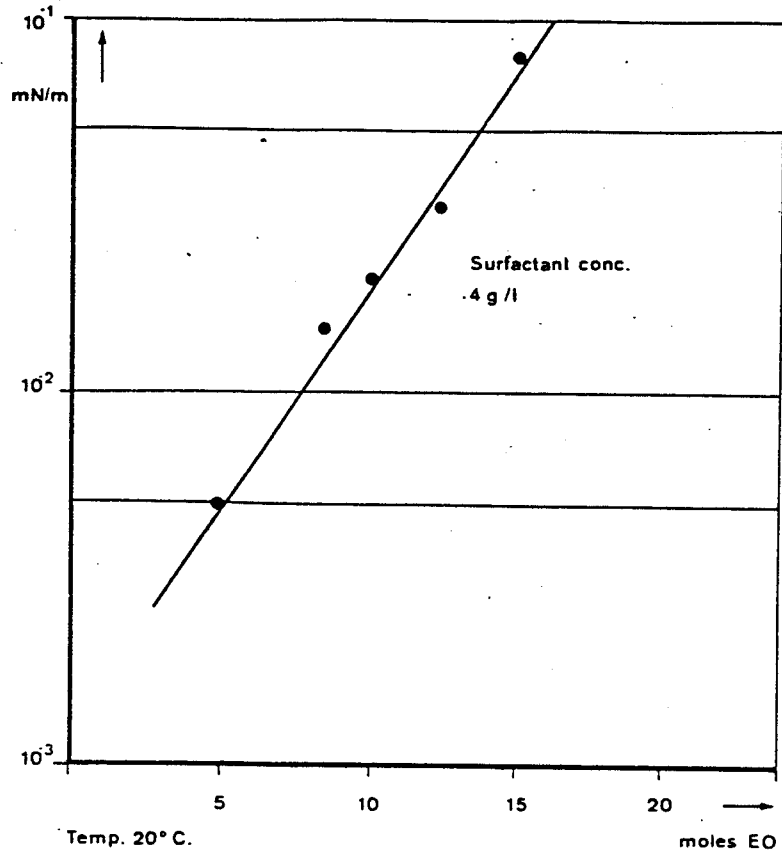


Fig. 1—Interfacial tension as function of number of moles EO

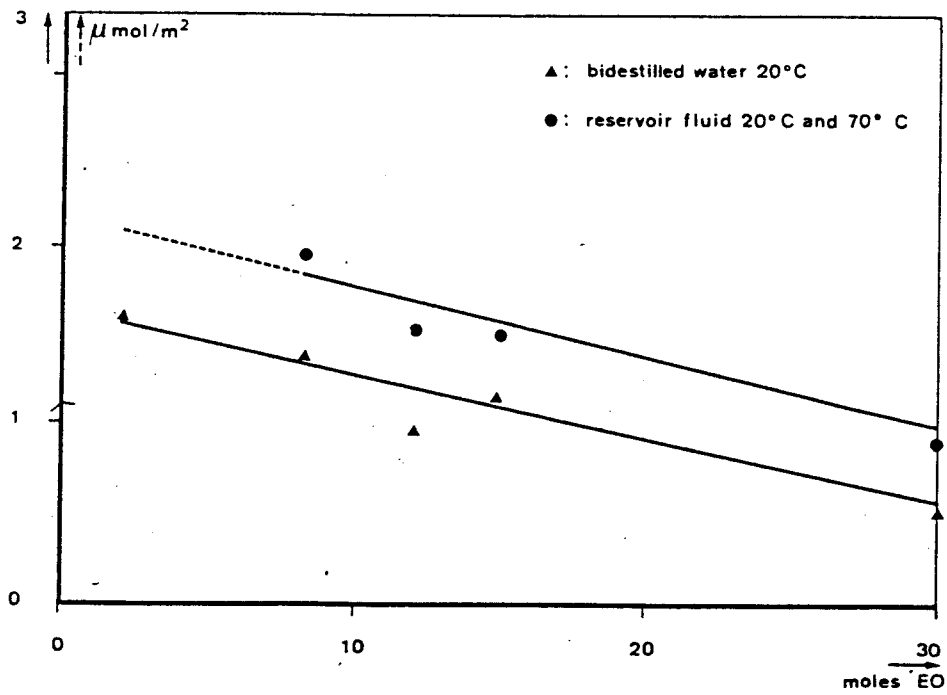


Fig. 2—Adsorption as function of number of moles EO



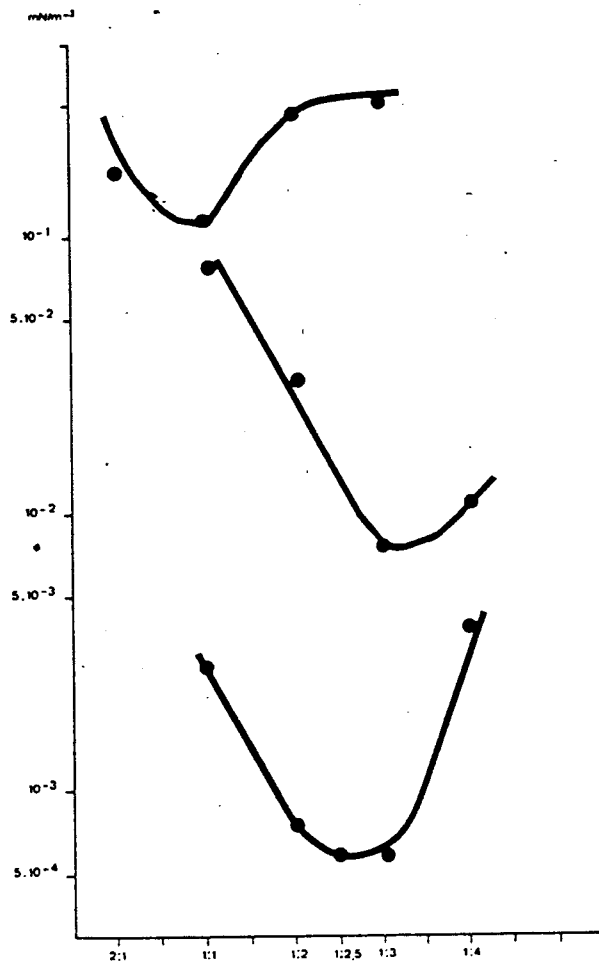


Fig. 3—Interfacial tension as function of conversion

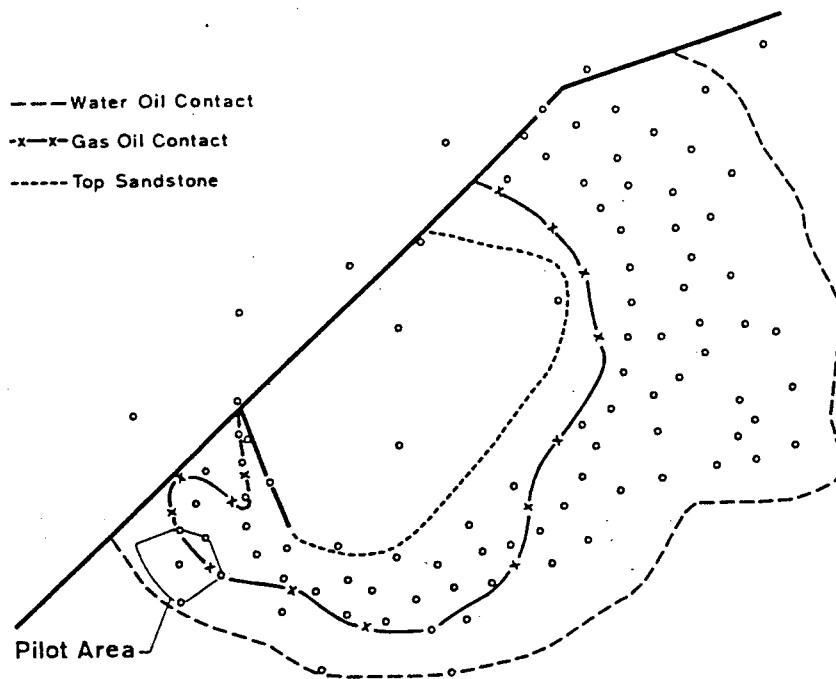


Fig. 4—Velebit oilfield

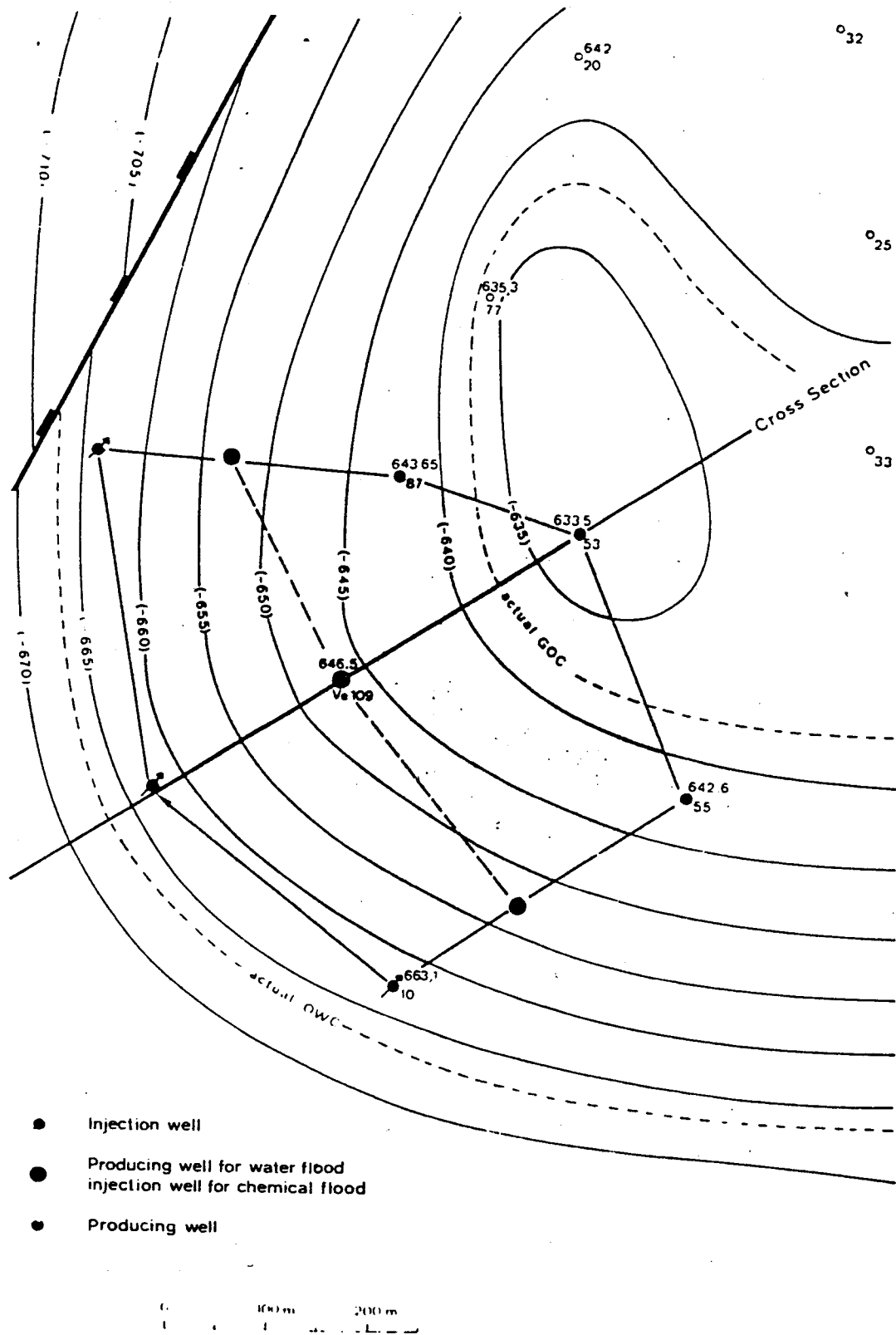


Fig. 5—Pilot area; flooding grid

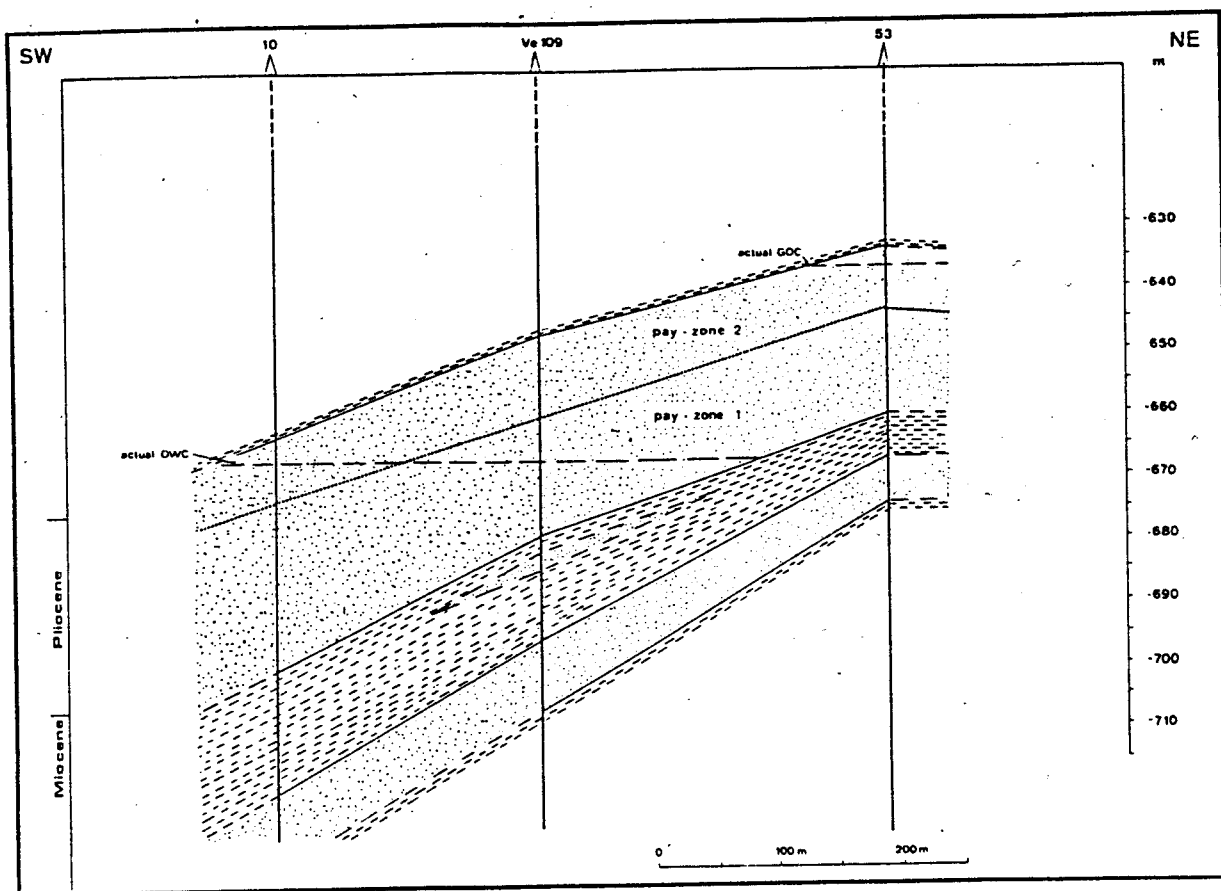


Fig. 6—Cross section of pilot area

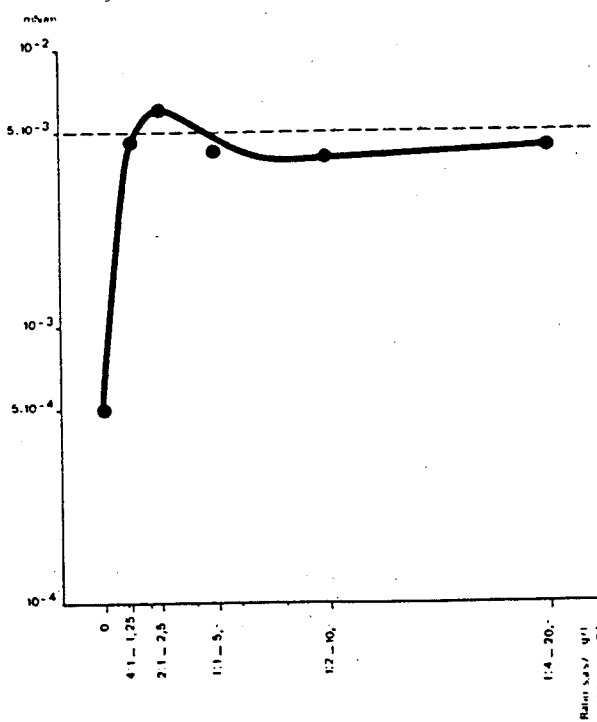


Fig. 7—Interfacial tension, influence of alcohol

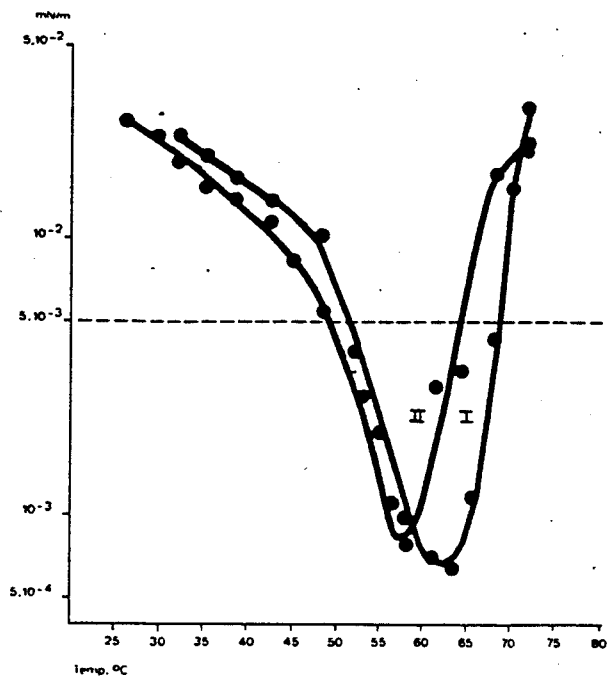


Fig. 8—Interfacial tension, influence of temperature

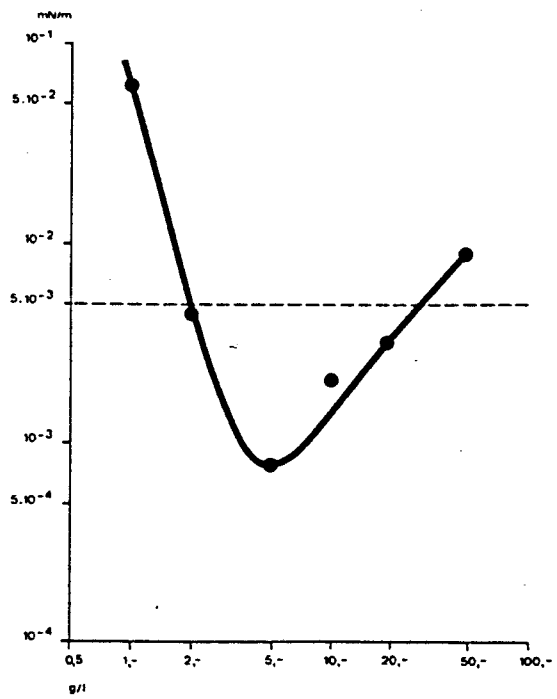


Fig. 9—Interfacial tension, influence of concentration

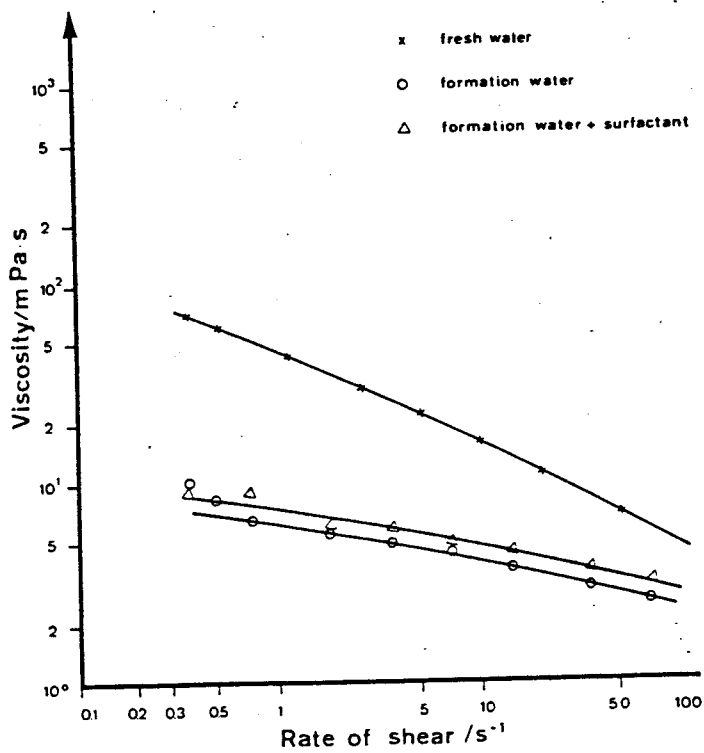


Fig. 10—Viscosity of a polyacrylamide

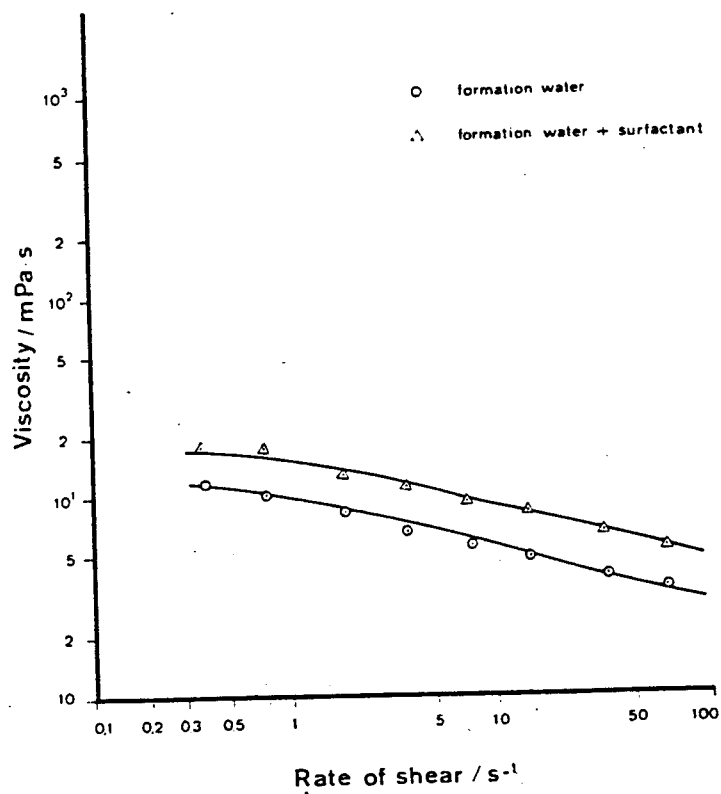


Fig. 11—Viscosity of a polysaccharide

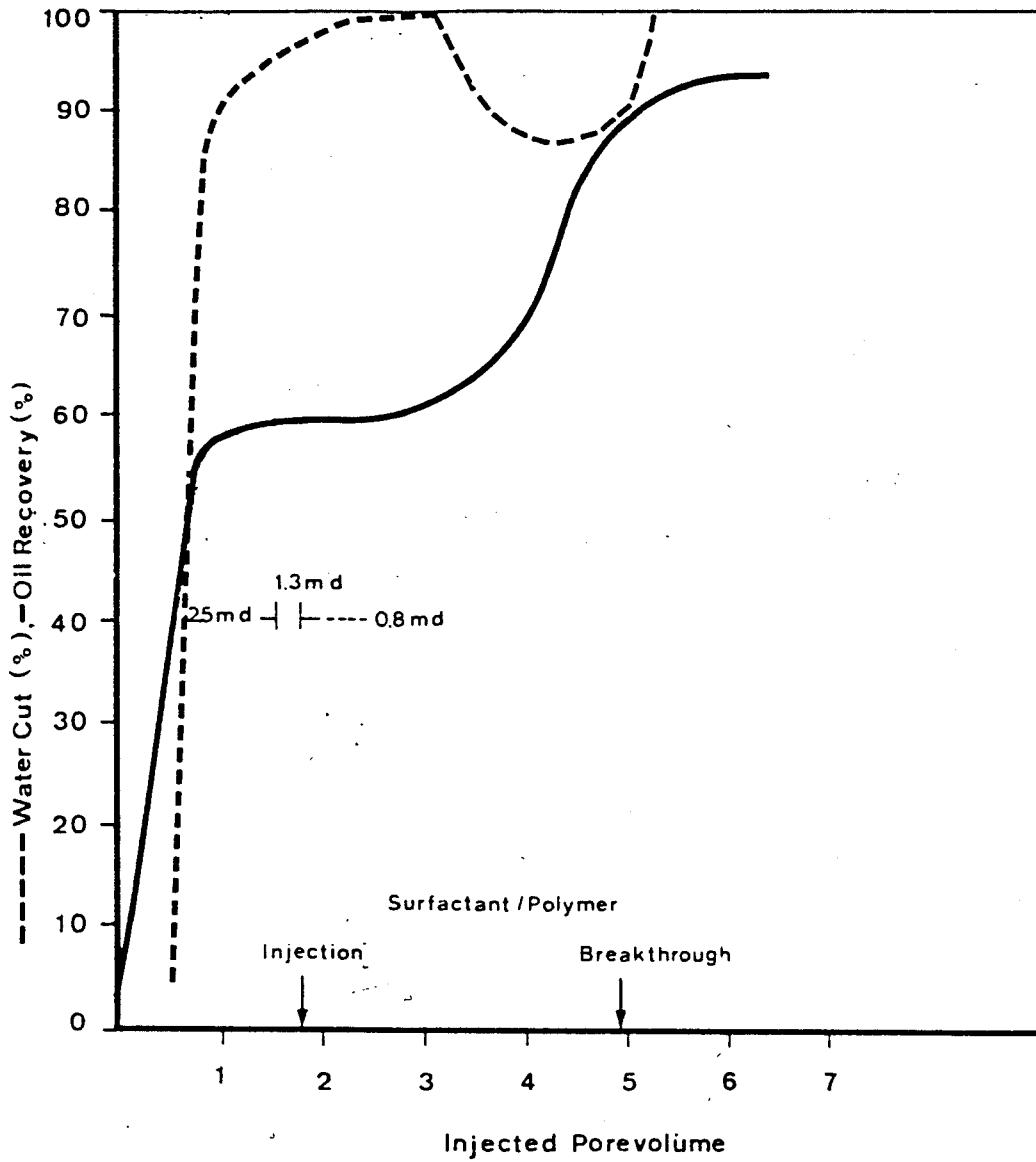


Fig. 12—Laboratory flooding test.