

POLYMERIC COMPOSITIONS TO INCREASE OIL RECOVERY

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ABSTRACT

The issues of synthesis of the study of the physicochemical properties of the modified polyacrylamide in the presence of gossypol resin and formalin are considered in this work. This polymer composite is supposed to be used for enhanced oil recovery. It was established that the synthesized polymer reagent has fairly satisfactory stability at high (over 200°C) temperatures and formation water salinity. the prospect of increasing oil recovery through the use of a polymer composition is aimed at solving the problem of maximizing oil recovery from wells. These studies are aimed at solving the problems facing oil production and treatment companies.

Keywords: Polymer Reagent, Oil Recovery, Viscosity, Modification, Polymer Flooding.

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INTRODUCTION

Oil is a main source of energy as well as an important raw material for the chemical industries.¹ The stages of oil field development are usually divided into three stages, which can be seen in the following figure (Fig.-1):

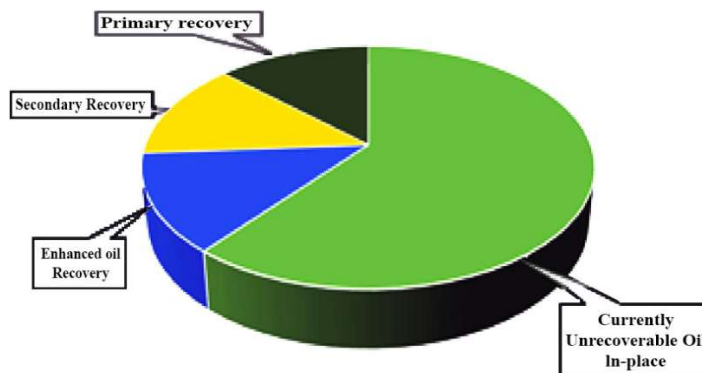


Fig.-1: Oil Production in Different Stages^{4,5}

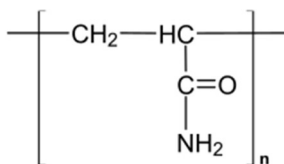
Today, many oil fields are in the final stage of development, which is characterized by a steady decrease in oil production, simultaneously with an increase in the volume of its water cut.^{3,4} The average degree of the water content of the produced oil in Kazakhstan is about 90 %. The capillary retained oil is displaced with the help of surfactant solutions and compositions on their basis. Unique physical and chemical properties of polymer-surfactant complexes cause their wide application in various branches, in particular as composite materials.⁶⁻⁸ One of the first polymers to be used in EOR was high molecular weight polyacrylamide.¹⁻⁵ Through its hydrodynamic volume, high Mw polyacrylamide boosted the displacing viscosity. In contrast to water flooding, temperature, and salt resistance could also be improved.⁹⁻¹¹ More than any other type of PAM, this type has been used in oilfields.

We consider that oil production should grow not only due to the commissioning of new fields but also due to an increase in oil recovery from exploited fields. The amount of residual oil in the number of fields is determined by tens and hundreds of millions of tons. At the same time, it should be noted that a slight

increase in oil recovery is equivalent to the discovery of several fields. Thus, the prospect of increasing oil recovery, i.e. solving the problem of maximum oil recovery from wells is one of the most important tasks facing the enterprise in the production and treatment of oil.⁶ The purpose of this work is to create new multifunctional compositions based on polyacrylamide and fatty acid distillation bottoms to displace hard-to-recover oil reserves. This paper presents the synthesis and properties of surfactant complexes modified polyacrylamide in the presence of gossypol resin and formalin. The physic-chemical properties of polymeric reagents were studied, and efficiency testing in the formation of water for oil displacement was carried out. The obtained polymer composites showed the best results required for applications with high salinity and high temperature of formation water.

EXPERIMENTAL

The oil from the Kumkol fields was used as the oil under study. Oil samples were taken with a density of 812–819 kg/m³. Water mineralization (calcium chloride) in the reservoirs was 49.7–84 g/l. A polymer composition based on polyacrylamide and distillation residues of fatty acids was used at drawing up the compositions. The modifying agent in this case is gossypol resin fatty acids. Gossypol resin is a VAT residue of vacuum distillation of fatty acids obtained from cotton soap stocks during the processing of cotton seeds and oil. It is a homogeneous viscous mass from dark brown to black. In this polymer composition polyacrylamide "Alita" from the Kazakhstan firm was used. Its chemical formula is as follows:



Obtaining fatty acids of gossypol resin was carried out by the method of polycondensation in an alkaline medium at a temperature of 80–90°C for 2–2.5 hours. In this case, polycondensation and saponification of naphthenic hydrocarbons and gossypol resin occur simultaneously. White spirit is introduced through a vacuum evaporator, followed by draining of these fractions for the extraction of unsaponifiable fractions. The resulting semi-product consists of 60–70% of sodium salts, mainly unsaturated fatty acids with a predominant fraction of C₁₁–C₁₇ i.e. (R-COOH).^{7,8} IR spectra were taken on a Shimadzu YRPrestige-21 IR-Fourier spectrometer with a Miracle attenuated total internal reflection attachment to establish the spectral characteristics of the modified polymer reagent. The Jeol JSM-6490I V electron microscope was used for the structural-elemental composition (REM). Further, DTA studies were carried out to determine the elemental composition of the obtained polymer reagents. The composition of the substance of the active part of the polymer reagent was determined by the morphologies of thermal curves and numerical values of the intensities of endo- and exothermic effects using the thermogravimetric readings of TG-lines associated with them. The differential thermal analysis method is based on the registration by the device of changes in the thermochemical and physical parameters of polymer reagents that can be caused when it is heated. The thermochemical state of the sample is described by curves: T (temperature), DTA (differential thermoanalytical), TG (thermogravimetric), and DTG (differential thermogravimetric), the last curve is a derivative of the TG function. The furnace heating mode is linear (dT/dt = 10 deg/min), and the reference substance is calcined Al₂O₃. The weight of the sample was 200 mg, with the sensitivity of the balance being 200 mg. The analysis was performed within the following limits of the instrument systems: DTA = 250 μV, DTG = 500 μV, TG = 500 μV, T = 500 μV. The purpose of the differential thermal and thermogravimetric analysis of the sample was to determine the composition of the thermally active part of the test sample and to reveal the thermal behavior of the sample under conditions of dynamic temperature rise. The analysis was carried out in the air, in the temperature range from 20 to 1000°C. The measurement of the viscosity of solutions of polymeric reagents was carried out in a Ubellode capillary viscometer with a hanging level (solvent outflow time ~ 100–120 seconds) at a temperature of 25±0.1°C. The temperature in the thermostat, in which the viscometer was installed, was maintained with an accuracy of ± 0.1 °C. The measurement accuracy of the reduced η_{pr.} viscosity was ±1%. The reduced viscosity of polymer solutions was determined depending on the concentration, temperature, pH of the medium, and electrical conductivity. The viscosity of selected samples of polymer solutions was measured to determine the optimal reaction time and

temperature. The effective viscosity of the selected samples of PAA solutions was measured on a rotational viscometer “Ofite 900 viscometer” at a shear rate $\gamma=6,20,60,100,300$ pr to determine the optimal reaction time and temperature of the modified PAA. The synthesized modified product based on PAA in the presence of gossypol resin and formalin was tested on rock samples (cores) using the UIK-S(2) core testing unit (Fig.-2).



Fig.-2: Installation of the Core Study UIK-S (2)

Piston pumps and pressure sensors were used for the core experiment, as well as a core holder in which the core sample was fixed with epoxy glue. The test methodology was as follows:

1. Evacuation of the model for 10 minutes;
2. Saturation of the model with water;
3. Displacement of water by oil until irreducible water saturation is reached;
4. Injection into the model of one pore (PV) volume of water to displace oil;
5. Injection of several software solutions of the polymer reagent.

A core with a diameter of 3 and a length of 4.6 cm, respectively, were used in the work. (Fig.-3).



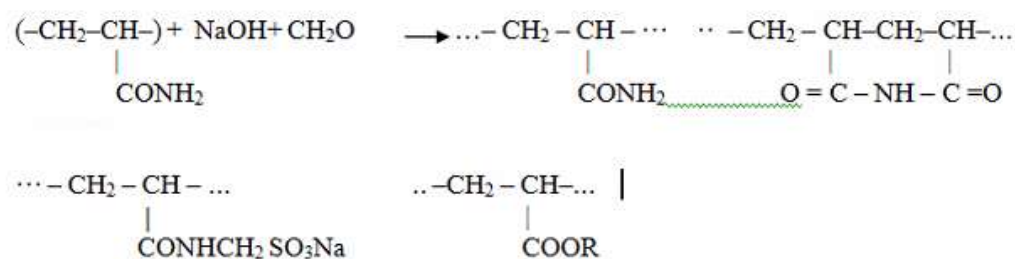
Fig.-3: Core Sample

RESULTS AND DISCUSSION

The production of composite polymeric surfactants based on modified polyacrylamide derivatives for enhanced oil recovery was carried out by hydrolysis, and sulfomethylation, followed by modification in the presence of gossypol resin fatty acids. The hydrolysis process is carried out with a 1-2% aqueous solution of sodium hydroxide, sulfomethylation is carried out in the presence of a 40% formalin solution in an amount of 10-20 ml and sodium sulphate, and modification of $10\text{-}20 \times 10^{-2}$ kg of fatty acids with gossypol resin.

The hydrolysis was carried out in the presence of fatty acids of gossypol resin in order to increase oil recovery. The modification process in the presence of gossypol resin fatty acids results in a decrease in viscosity. Cross-linking (of the unreacted and oligomeric fraction of gossypol resin fatty acids with PAA) was carried out in the presence of an initiator of the reduction-oxidation system (potassium persulfate and sodium sulphate 0.1% by weight), at a temperature of 40-60°C within 1.0 hour to increase the viscosity and high molecular weight fraction in the macromolecule. The viscous mass turns into a gel state, and a high

yield of the high molecular weight fraction is observed (the relative viscosity of a 1% modified PAA solution is 5.9 mm²/s, and after crosslinking it is 11.5) as a result of cross-linking. Sequential carrying out of hydrolysis processes and modification of PAA, i.e. the resulting carboxyl groups interact with the fatty acids of the gossypol resin according to the reaction:



Where R is fatty acid residues of gossypol resin (C₁₁-C₁₇-COOH)

An intense absorption band at 3100-2850 cm⁻¹, which corresponds to the -S-H and ≡C-H stretching vibrations of the -NH group involved in the hydrogen bond of aliphatic compounds is observed in the IR spectrum of the studied sample of the modified polymer (Fig.-4). There is also an absorption band with low wavelength intensities of C-O-C compounds present in esters, which belongs to the acetate group at 1350-1030 cm⁻¹. IR spectra with a wavelength of low intensity 1969-1813 cm⁻¹ characterize stretching vibrations =C=O of non-conjugated types of bonds in amides, and absorption bands 1700-1530 cm⁻¹ correspond to stretching vibrations =C=C.⁴

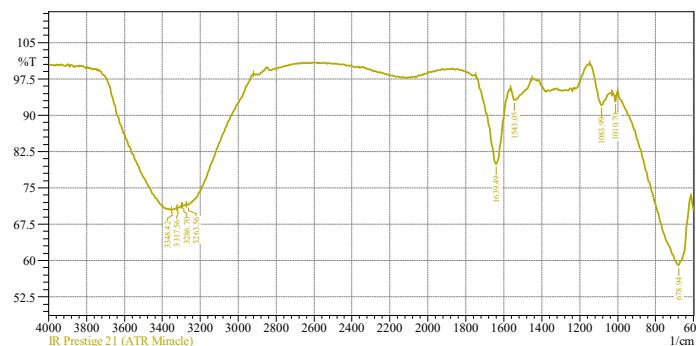


Fig.-4: IR spectrum of Hydrolyzed Polyacrylamide and Formalin in the Presence of Gossypol Resin Fatty Acids

The presence of carboxylate and amide groups was established, and it should also be noted that an increase in their composition of densely located carboxyl groups along the chain of the macromolecule as a result of studies of the IR spectra of the synthesized polymers.

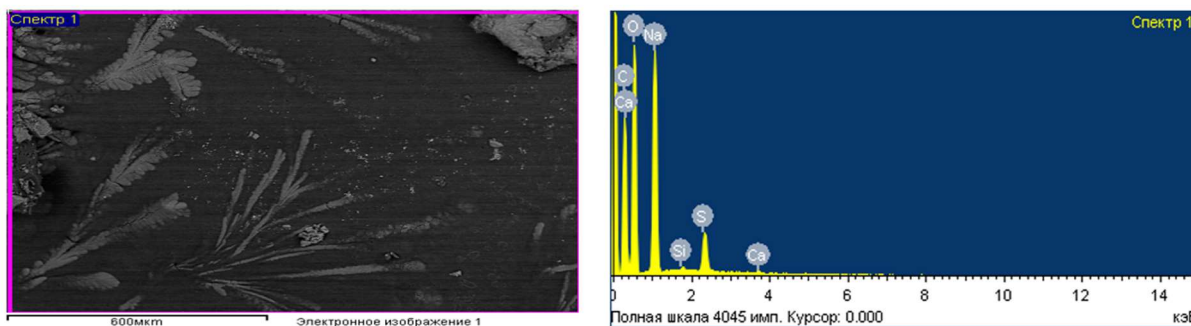


Fig.-5: Elemental composition of Hydrolyzed Polyacrylamide and Formalin in the Presence of Gossypol Resin Fatty Acids

Thus, the analysis of IR spectra showed that the resulting modified composite polymer based on polyacrylamide and formalin in the presence of gossypol resin fatty acids contains functional groups: -COO⁻; CH₃; NH₂⁺; -SO₃⁻. The presence of the following elements as shown: - 39.04%, O - 40.73%, Na -

20.78%, Si - 0.14%, and S - 3.85% as a result of the elemental and mineralogical composition of the resulting polymer composite (Fig.-5). The selection of the ratio of monomers and modification conditions ensures a high conversion of monomers, which increases the yield of the final product. The synthesized polymer throughout the structure has an amphiphilic structure, macromolecules, which contain a hydrophobic group and a hydrophilic part, they are able to adsorb and reduce the interfacial free energy, which allows them to be classified as high-molecular surfactants.²⁻⁴ The establishment of the equilibrium rate in the adsorption layer depends on the flexibility (rigidity) of the chain of macromolecules, their structure, and functional composition, and is due either to the diffusion of macromolecules to the phase boundary or to dehydration and relaxation processes that occur in the adsorbed layer itself, in addition, the possibility of joint action of these factors is not ruled out.⁴ The measurement of the surface tension of the obtained polymers based on hydrolyzed polyacrylamide and fatty acids shows that the decrease in the surface tension of water is explained by the ability of macromolecules to orient and associate in the adsorption layer in the presence of high-molecular surfactants at the water-air interface.⁹ The conducted studies have shown that the surface tension of solutions of polymeric reagents (Table-1) is decreased with increasing concentration. This is apparently due to the different content of surface-active units.

Table-1: Obtained Data on the Surface Tension of Polymeric Reagents

Polymers	Concentration, kg/m ³	Surface tension ($\sigma \cdot 10^{-3}$ N/m) of solutions
Polymer reagent	0,1256	55,06
	0,03125	51,41
	0,0625	49,48
	0,1265	46,61
	0,25	42,79
	0,5	41,67

The concentration of particles ϕ (volume fraction) and the potential of pair interaction of particles are the main factors that determine the structure and rheological properties of dispersed systems. The particles retain complete freedom of movement, which determines the absence of structure in dilute aggregative-ly stable systems. The viscosity of such systems is calculated by the Einstein formula: $\eta = \eta_0(1 + \alpha \times \phi)$, where η_0 is the viscosity of the medium; α is a coefficient equal to 2.5 for spherical particles with their free rotation in the flow. Next, the dependence of effective viscosity on shear stress was studied (Fig.-6) to determine the relationship between the chemical composition and rheological properties of aqueous solutions of the synthesized water-soluble polyelectrolytes. The intensity of intermolecular interaction of macromolecules in solutions of synthesized modified polymers is estimated using the temperature coefficient of viscosity of undestroyed structures. Rheological studies made it possible to determine the structurization of aqueous solutions of the synthesized modified water-soluble polymer reagent.¹²⁻¹⁵

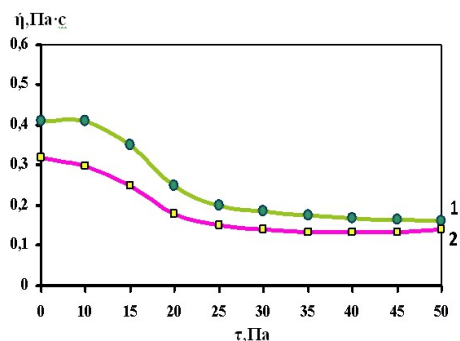


Fig.-6: Dependence of the effective viscosity η (Pa s) of aqueous solutions (4%) of the studied polymer reagent on the shear stress τ (Pa)

1- Saponified PAA with sodium hydroxide in the presence of sodium sulfate formalin (2) and fatty acids of gossypol resin (1).

The polymer reagent, when dynamically heated from 20 to 1000°C, left a series of endo- and exothermic effects on its thermal curves associated with the decomposition of its structure. The most intensive degradation of the polymer reagent was traced in the initial part (20-180°C) of the general heating temperature range. The differential thermoanalytical (DTA) and thermogravimetric (DTG) curves left very deep peaks at 100 and 90°C in the specified temperature range, associated with the release of a significant amount of aromatic substance into the atmosphere (Fig.-7).

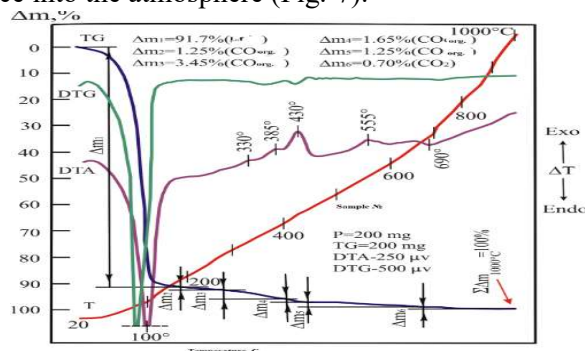


Fig.-7: Derivatogram of Modified PAA in the Presence of Gossypol Resin and Formalin

Table-2: Thermogravimetric Indicators of the Polymer Reagent Within 20-1000 °C

Weight Loss Sequence	Amount of weight loss, in %	Volatile components of the heated sample	Decomposition stage temperature range, °C
Δm_1	91,7	L.F.	20-185
Δm_2	1,25	CO_{org}	185-280
Δm_3	3,45	CO_{org}	280-400
Δm_4	1,65	CO_{org}	400-445
Δm_5	1,25	CO_{org}	445-670
Δm_6	0,70	CO_2	670-855
$\Sigma \Delta m_{1000^\circ C}$	100	L.F., CO_{org} , CO_2	20-1000

Note: L.F. – a light fraction

Further heating of the sample (180-285°C) leads to a monotonous decrease in the weight of the sample, due to the release of sabot-bound compounds - CO_{org} . The amount of the specified substance does not exceed 1.25% of the initial weight of the sample. The remaining emissions (Δm_1 , Δm_2 , and Δm_3) are caused by the combustion of a relatively “heavy” fraction of organic matter (OM), leaving small but clearly pronounced exothermic effects on the DTA curve at 330, 385, 430, and 555°C, Fig.-8, Table-2. The sample left a weakly developed endothermic effect on the DTA curve in the final part of the thermal decomposition (670-855°C). The developed high-molecular-weight polymeric surfactants were tested on the UIK-S (2) core research unit in experimental laboratory conditions (on a geological model of simulating oil wells) to evaluate their effectiveness (Fig.-3). Oil, water, and polymer solution were pumped at a flow rate of 0.1 cm³/min. The experiment was carried out at room temperature. The porosity of the sample was measured by saturating it with water after vacuuming and is equal to 22%. The sample water permeability is at 100%. Water saturation was measured by filtering water through the sample at rates of 0.1, 0.25, and 0.5 cm³/min (Table-3).

Table-3: Water Saturation at Flow Rates 0.1, 0.25, and 0.5 cm³/min

Consumption, cm ³ /min	Inlet side pressure, MPa	Pressure in the center, MPa	Temperature, C	Permeability, mD	Average permeability, mD
0.5	0.184	0.091	28	2.4	2.15
0.25	0.105	0.045	28	2.14	
0.1	0.047	0.023	29	1.91	

The change in the oil displacement factor depending on the mass of the produced fluid, when water and 0.4% concentrated polymer reagent solution are injected into the core, is presented in Fig.-8 below. As can

be seen from the graph, the injection of the polymer reagent solution made it possible to increase the oil displacement efficiency by 7%.

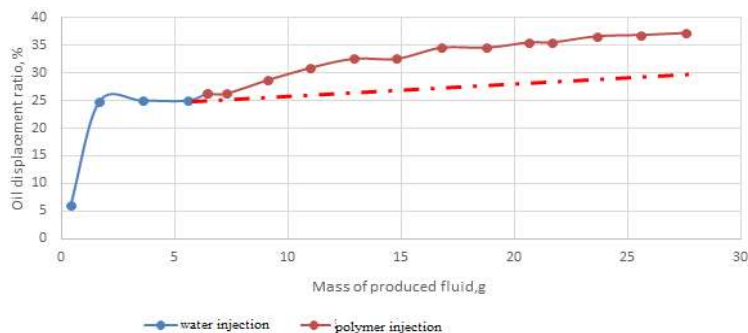


Fig.-8: Oil Displacement Factor Depending on the Volume of Produced Liquid

CONCLUSION

Thus, the conditions for obtaining a polymeric reagent based on modified PAA in the presence of gossypol resin and formalin were determined for using enhanced oil recovery. A mechanism for oil displacement under the action of a polymeric reagent in bench conditions is proposed¹⁶⁻¹⁸. The optimal conditions for the process of obtaining a polymer reagent based on polyacrylamide in the presence of gossypol resin and formalin were revealed. The obtained data will make it possible to model the process of displacement of residual high-viscosity oil from an inhomogeneous porous medium. The effect of temperature, concentration, pH of the medium, and the degree of water mineralization on the process of obtaining a polymer reagent in composite disperse systems was studied. It was established that the synthesized polymer reagent based on modified PAA in the presence of gossypol resin and formalin has fairly satisfactory stability at high (over 200°C) temperatures and formation water salinity. The resulting composite polymeric reagent during the displacement of oil from the Kumkol field gives the best results, that is, the injection of a polymeric reagent solution made it possible to increase the oil displacement efficiency by 7%.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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