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Trends and Prospects of Physicochemical Methods for Enhanced Oil Recovery of Heavy Oil Fields

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Abstract

The main challenge of the exploitation of fields with hard to recover reserves including high-viscosity oil pools is a low oil recovery factor (ORF) in the development by the main impact, i.e. displacement agent and heat-carrier injection. The review considers trends and prospects of physicochemical methods for enhanced oil recovery (EOR) of high viscosity heavy oil fields developed in the natural mode and combined with thermal techniques. The main sources of the relevant information are proceedings of world congresses and annual international conferences for heavy oil recovery issues in countries with significant geological reserves of heavy oil and bitumen. The development and use of physicochemical EOR methods for that are grounded on nanoheterogeneous chemically evolving surfactant-based systems, both as cold technologies and combined with thermal steam stimulation (TSS), appear to be promising as one of the possible solutions to this problem. The perspective of the concept of chemically evolving oil-displacing systems is proven by field test results of EOR technologies developed at the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences Tomsk.

Keywords: heavy high-viscosity oil, enhanced oil recovery, thermal techniques, physicochemical methods, chemically evolving and surfactant systems, coordination compounds, polyols, field test

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INTRODUCTION

According to prognosis evaluation, unabated demand of the world economy for hydrocarbons will be met by the development of resources of new oil-producing regions, mainly in the northern region of the planet, and also through the exploitation of heavy high-viscosity oil and bitumen deposits [1, 2].

Crude oil is traditionally classified as light, medium, or heavy depending on its density expressed in kg/m^3 in SI or API degrees. In particular, the US Geological Survey classifies oil as follows: light oil density above 31.1°API (less than $870 \text{ kg}/\text{m}^3$); average – in the $31.1\text{--}22.3^\circ\text{API}$ range ($870\text{--}920 \text{ kg}/\text{m}^3$); heavy – in the $22.3\text{--}10.0^\circ\text{API}$ interval ($920\text{--}1000 \text{ kg}/\text{m}^3$); super – below 10.0°API (more than $1000 \text{ kg}/\text{m}^3$). The density of bitumen from fields in the Albert area (Canada) is about 8°API ($1010 \text{ kg}/\text{m}^3$).

World heavy oil reserves are about 5 times higher than the volume of residual recoverable reserves of light oil of low and medium viscosity, according to expert estimates – 810 and 162 billion tons, respectively. Canada, Venezuela, Mexico, USA, Russia, Kuwait, and China have large of heavy high-viscosity oil reserves (Fig. 1) [3–5]. In Russia, they are concentrated in the Komi Republic, Tatarstan, and Tyumen region. The volume of industrial reserves in

terrigenous rocks is about 4 billion tons (64 %), in carbonate basins – 2.3 billion tons, or 36 % of the total reserves. The average annual total volume of heavy oil production in the world is close to 500 million tons, and the accumulated recovery is higher than 14 billion tons. Currently, heavy high-viscosity oil is considered as the main reserve of world oil production, which determines the relevance of fundamental and applied research work on forming new approaches to solving the problems of their extraction [4–10].

The main challenge of the exploitation of heavy oil fields lies in the fact that natural thermobaric conditions, *i.e.* low seam temperatures and pressures, do not ensure the required mobility of high-viscosity oil, on which the completeness of its recovery on the natural mode of development depends on. The use of various systems to maintain reservoir pressure, *i.e.* the water flooding and the injection of air and gases, is inefficient, as field production efficiency sharply reduces because of a large difference in viscosities of displacement agent and oil. During displacing high-viscosity oil with water, low-viscosity liquid or gaseous fluid, the viscous instability of displacement front appears and as a consequence, non-piston displacement mode is formed, which leads to a premature breakthrough of the displacing

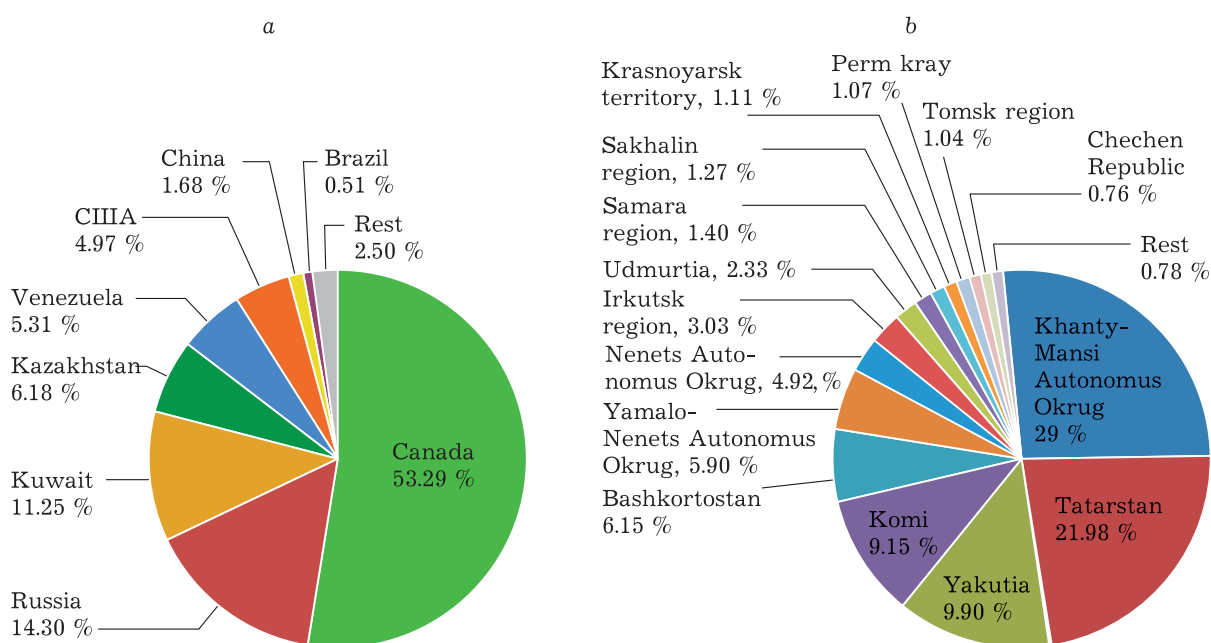


Fig. 1. Heavy viscous oil distribution in the world (a) and Russia (b) [3].

agent into the producing wells. As a result, the sweep efficiency of the productive reservoir by the applied impact is significantly reduced. On average, the final recovery factor of heavy oil by traditional non-thermal methods is not higher than 10–15 % of the field's balance reserves.

THERMAL METHODS OF ENHANCED OIL RECOVERY

To address the problem of enhanced oil recovery of heavy and high-viscosity oil pools, there is offered a wide range of various techniques [11–23]. The most common methods of enhanced oil recovery of heavy oil pools are thermal procedures grounded on oil viscosity decrease during heating, which results in an increase of its mobility under reservoir conditions.

There is intensive theoretical and experimental research on various options of thermal exposure that use the injection of water vapour and hot water, and also processes of intra-layer dry and wet combustion, thermochemical heat generation due to reactions with reservoir water and rock, microwave heating, and heat from geothermal sources.

Among thermal techniques, the method of steam treatment by stationary or cyclic vapour injection is most efficient and reached the stage of large-scale industrial application. The procedure is continuously developed, in other words, designs of steam injection wells are being improved, new thermal-stream techniques, in particular, the SAGD steam-gravity drainage system and its numerous modifications, have appeared. Steam generators and ground steam distribution systems are being improved. The steam that has dryness of 70–80 % in the wellhead and temperatures from 310 to 320 °C is typically injected. The injection pressure is not higher than 15–18 MPa. During burning 1 t of oil in a steam generator, 10 to 15 t of steam is produced. Treatments are considered effective if 1 t of oil is additionally extracted per 3–4 t of steam. The first cycle is the most effective. The efficiency of subsequent cycles is reduced almost inversely to the sequence number of the cycle.

Thermal steam stimulation is a technologically-difficult and high-cost development system. Therefore, it is promising to explore opportunity use of physicochemical methods to intensify the development and enhance oil recovery of heavy and high-viscosity oil pools as

non-thermal cold techniques and combined with TSS [24–27].

COMPLEX PHYSICOCHEMICAL AND THERMAL TECHNIQUES

Currently, opportunities to increase the efficiency of stream methods by combination with physicochemical techniques are being intensively explored in laboratory research and field pilot projects. Within this approach, additives of carbon dioxide, light hydrocarbon solvents, and non-condensable gases to water vapour are investigated. To line up water vapour input profile, there is used the alternate injection of foam and vapour. The foam is produced directly in a reservoir by the consecutive injection of non-condensable gas, in particular, nitrogen and an aqueous solution of thermally stable surfactants. Alkanes from propane to hexane are used as water vapour additives and in the alternating combination of light hydrocarbon solvents therewith. Aromatic solvents, such as benzene and toluene, are much more efficient solvents for heavy oil and bitumen, however, their use is constrained by fears of serious environmental risks due to their own toxicity and products of their natural degradation.

The combined injection of carbon dioxide and water vapour gives a substantial operational benefit; however, this technique has received industrial applications only in several deposits of North America, where there are carbon dioxide pools next to heavy oil fields.

The main problem of using carbon dioxide is severe CO₂ corrosion of metals and alloys of ground and downhole equipment. Nevertheless, research continues into an opportunity to use carbon dioxide of technogenic origin, in particular, from flue gases. Moreover, there is a stimulus towards it as international agreements to limit greenhouse gas emissions into the atmosphere. The use of chemicals forming carbon dioxide during heating directly in the reservoir together with the vapour is promising. This technique is widely used in oil-displacing systems of the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences (IPC SB RAS) [6, 27]. Carbamide included in their composition is hydrolyzed in an aqueous solution during heating to 70 °C and above turning into carbon dioxide and ammonia. One tonne of carbamide

yields 373 m³ of carbon dioxide and 747 m³ of ammonia. Carbon dioxide mainly dissolves in oil, resulting in its viscosity decrease, and this, in turn, causes a favourable change in the ratio of the mobility of oil and the aqueous phase. The technologies of IPC SB RAS using carbamide-containing oil-displacing and gel-forming compositions are industrially applied in Russia in the fields of Western Siberia, Permian-Carboniferous deposit of Usinsk oilfield in the Republic of Komi, and have been successfully tested at heavy oil fields in China and Germany [27–31].

THERMOTROPIC GELS TO ENHANCE OIL RECOVERY AND LIMIT WATER PRODUCTION

The IPC SB RAS has been exploring physicochemical and hydrodynamic aspects of *in situ* gel formation for a number of years. There were investigated the kinetics of gel formation, phase equilibria, rheological and filtration properties of thermotropic gel-forming systems: polymer systems with lower critical dissolution temperature based on cellulose ethers (CE), inorganic systems, such as aluminium salt – carbamide – surfactant – water, *etc.* [22–24, 27–31]. Thermotropic gel-forming systems are low-viscosity aqueous solutions under surface conditions and turn into gels under reservoir conditions. Gel formation proceeds under the

influence of thermal energy of the reservoir or injected heat carrier.

As demonstrated by the exploration of gel-forming ability of thermotropic systems by rotational viscometry methods in the temperature range from 20 to 150 °C and a pressure to 50 atm with hydrostatic compression under dynamic conditions; at a certain temperature, the solution turns into a solid-like gel of coagulation structure with pronounced thixotropy and a yield stress of 25–90 Pa (Fig. 2).

A yield stress value increases with the enhanced loading rate. The type of rheological dependences indicates the viscoelastic properties of gels. It is worth noting that in the shear rate range of 0.01–5 s⁻¹ at high pressures, under hydrostatic compression conditions, shear stress and viscosity of gels in aluminium salt – carbamide – water and EC-water systems have values of several orders of magnitude higher than at atmospheric pressure (see Fig. 2). Gel formation temperature and time may be monitored by additives of electrolytes and non-electrolytes (for example, Fig. 2, b). The gels are stable and retain their rheological characteristics at high temperatures – to 150–200 °C. Based on the results of the exploration of the kinetics of gel formation and rheological characteristics of aluminium salt – carbamide – water – surfactant and EC – carbamide – water systems, GALKA[®] and NINKA[®] gel forming systems with

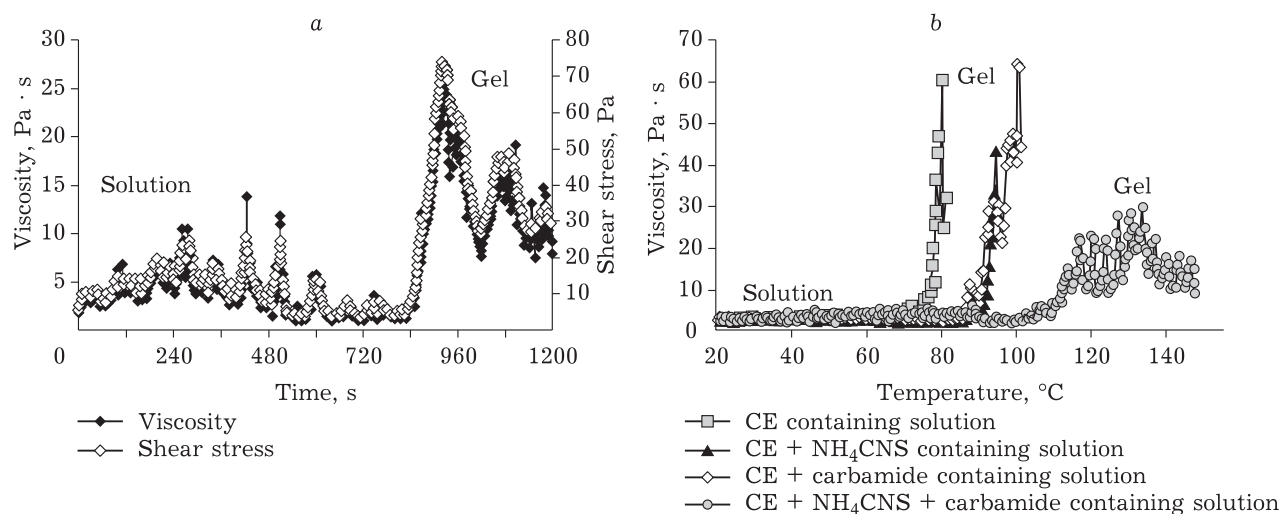


Fig 2. Viscosity change at a shear rate of 3 s⁻¹ in thermotropic gel-forming systems: aluminium salt – carbamide – water during thermostating at $T = 150$ °C (a) and a polymer with lower critical dissolution temperature (a cellulose ether) – water in solution – gel phase transition (b).

different gel formation time (from several minutes to several days) were developed in the 30–320 °C temperature range. Their use allows developing deflector screens in the reservoir, monitoring filtration flows, which results in increased oil production, and decreased water content of products.

The field test of the technologies was carried out in Permian–Carboniferous deposit of Usinsk field (Komi) at the late stage of the development was carried out in 2002–2006. The technologies have been used on an industrial scale since 2007. In 2014–2017, 185 wells were processed according to integrated technologies. Furthermore, additional oil production upon thermal-stream and cyclic steam exposure was over 800.000 t using GALKA[®] gel forming systems. The use of gels at a real influence leads to increased coverage of the reservoir by steam injection, decreased water cut of products by 3–45 %, daily oil production increase by 11–33 %, and liquid flow rate decrease by 14–25 %. Upon cyclic steam stimulation (CSS), oil production increase was from 3 to 24 t/day per well, additional oil production – an average of 980 t per well-processing. Pilot tests of GALKA[®] systems have been successfully carried out in the fields of China, Vietnam, and Germany.

The field test of the technology of selective limitation of water inflow limitation upon vapour areal injection was carried out for 5 producing wells of Usinsk field in 2014 using METKA[®] thermoreversible gel-forming system. The technology demonstrated a high efficiency. After the injection of METKA[®] system, there is an oil flow rate increase and decreased water cut of products. Additional oil production is ~11000 t, or 2100 t per well. The duration of the treatment effect is 16 months. The technology is recommended for industrial use. Field tests of the METKA[®] systems were successfully carried out in the fields of China, Vietnam, and Oman.

In the development of these works to water shut-off and increase oil recovery of high-viscosity oil fields during flooding, steam and steam cycle action in the temperature range of 60–220 °C, the IPC SB RAS developed MEGA high-temperature gel-forming system with two gel-forming components (polymeric and inorganic) based on the aluminium salt – simple cellulose ether – carbamide – water system formed directly in the reservoir, and connected nanoscale structures of the type gel

in gel with improved rheological characteristics and structural and mechanical properties. The factor that causes gel formation is the thermal energy of the formation or injected heat-carrier, without a cross-linking agent. During heating cellulose ether in the system above lower critical dissolution temperature, a polymer gel is formed due to the phase transition, and then inside the polymer gel by the mechanism of hydrolytic polycondensation initiated by the products of carbamide hydrolysis, an aluminium hydroxide gel is formed, that is, the structure of gel in gel. As a result, the structural and mechanical properties of the gel are improved, its viscosity and elasticity increase significantly. The gels formed in the reservoir constrain the water or steam breakthrough from injection to production wells and redistribute the filtration flows of reservoir fluids in the oil reservoir, which leads to the stabilization or a decrease of the water content of the surrounding producing or steam-cycle wells, and increased oil production.

The first pilot work according to the technology using the MEGA gel-forming nanostructured system to limit water inflow and increase oil recovery was successfully carried out 2016–2017 for 9 producing wells in Permian–Carboniferous deposit of Usinsk field upon cyclic steam stimulation and steam flooding. The volume of the injected system was 80–120 m³ per well. After processing wells there is significant water cut decrease, by 12–40 %, and multiple oil flow rate increase (Fig. 3). The technology is recommended for industrial use.

COLD TECHNOLOGIES

The practice has demonstrated that the efficiency of TSS decreases with decreasing the thickness of the reservoir and increasing its inhomogeneity and compartmentalization mainly due to unproductive heat loss through the roof and the bottom of the reservoir, and also in the case where the latter is composed of unconsolidated, uncemented sandstone, easily destroyed by steam injection. Physicochemical technologies used together with TSS and independently as cold technologies are promising in this situation [24–26].

In cold technologies, it is possible to use various principles of impact on high-viscosity

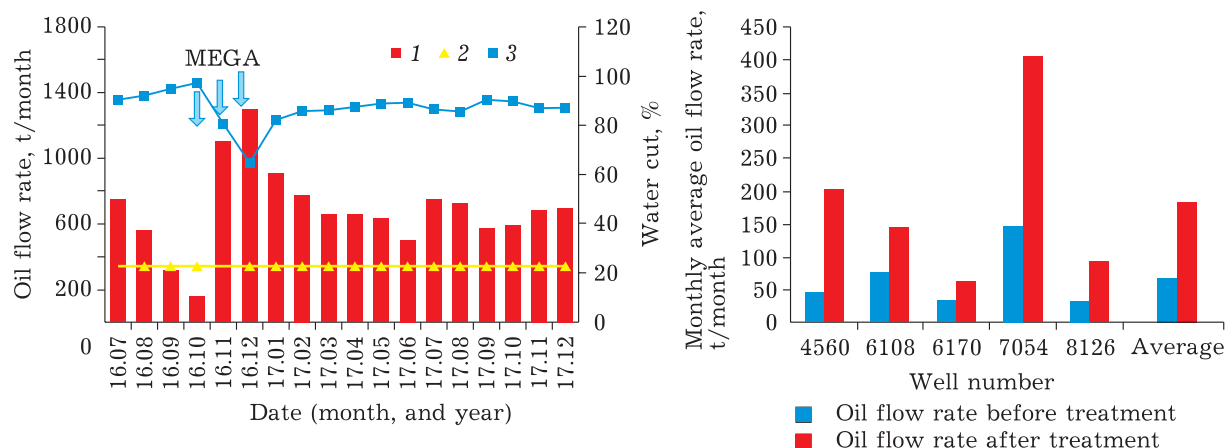


Fig. 3. Water shut-off using MEGA systems in total along 5 producing wells at Permian-Carboniferous deposit of Usinsk field, 2016–2017: oil flow rate increase and water cut decrease. : 1 – oil flow rate, 2 – average for 2016 (before treatment), 3 – watercut.

oil and the reservoir rock comprising it: injection of light gaseous or liquid hydrocarbons mixing with oil, sometimes with additives of polar co-solvents, in particular, the Vapex process, of liquid composite systems that transfer oil into a state of low-viscosity direct emulsion or solving the rock. Among these technologies are also vibrowave and vibroseismic impacts that affect the phase state and rheology of heavy oil. Great attention is paid to microbiological exposure on high-viscosity oil reservoirs. Cold high-viscosity oil production (CHOPS) from poorly cemented sand rock of the collector as a mixture with sand is industrially used and continues to be developed. It is carried out due to maintaining depression for the reservoir, sufficient to destroy the bottomhole zone to form a fractal network of extended cavities, *i.e.* wormholes, due to the removal of sand and wells significantly increasing the flow rate.

Large reserves of enhanced oil recovery of heavy oil pools may be implemented due to the use of cold physicochemical technologies, in particular, by the injection of various systems of chemicals into producing reservoirs. Some of them that are surfactants, solvents, carbon dioxide, *etc.* allow partially or completely eliminating the negative impact of capillary forces. Others change rheological properties and structure of filtration flows of formation fluids and reduce hydrodynamic anisotropy of the reservoir (polymer solutions, sols, gels, emulsions, and foams).

Oil remaining in the reservoir after flooding is referred to as residual. According to expert estimates, the remaining reserves are classified as follows [32]:

oil remaining in low-permeability interlayers and sections not covered by water – 27 %;

oil in stagnant zones of homogeneous reservoirs – 19 %;

oil remaining in the lens and is impervious screens untapped by wells – 24 %;

capillary-retained droplets and film oil – 30 %.

The oil reservoir has a very developed interface. Therefore, capillary-retained and film oil remaining in the reservoir after flooding is not less than 30 % of all residual reserves representing the main object for cold physicochemical technologies. As demonstrated by the experiment, to produce the residual oil, a systemic reliable approach to enhanced oil recovery (EOR) methods that allows arranging in a certain order and bringing into step various types of impacts on series of producing and injection wells is extremely important [23–34].

Currently, out of chemical cold technologies, polymer-alkaline flooding and waterflooding with the use of microemulsions are being intensively explored [35, 36]. These technologies have a long history, originally being created to increase oil recovery of light oil fields [37–39]. However, with the appearance of new polymers and surfactants, interest in them has revived, especially in the application to heavy oils.

POLYMER/ALKALINE AND MICROEMULSION FLOODING

According to the opinion of many researchers, alkali-surfactant-polymer (ASP) flooding is one of the most attractive chemical methods of enhanced oil recovery. In ASP systems, the alkali and the surfactant ensure ultra-low interfacial tension in the reservoir at the boundary with the displaced oil, while the polymer ensures good mobility control and maintains the piston displacement mode. Nevertheless, in practice, ASP efficiency, especially for heavy oil pools with carbonate reservoir rock proved to be much lower than expected mainly because of rock hydrophobicity and high mineralization of reservoir water of chloride-calcium type, typical for heavy oil pools. The presence of the divalent Ca^{2+} and Mg^{2+} cations in the formation brine results in the decomposition or precipitation of surfactants and especially polymers during the inevitable mixing of the alkaline system with the displaced oil and reservoir water during displacing. Currently, the primary effort of researchers is aimed at the elimination of the indicated negative phenomena, firstly, by the development of salt-resistant forms of reagents and secondly, by the alternation of the injection system portions and fresh water in order to avoid or minimize the negative effects of contacts of the system with reservoir water.

The key point of application of microemulsion oil-displacing systems is their ability to generate ultra-low interfacial tension both on the borderline with oil and with reservoir water [37, 38]. Within the theory of immiscible displacement, this provides a great value of the capillary number that is a criterion for system effectiveness, its ability to reduce the residual oil saturation by additional washing the capillary-retained drop and film oil. A key aspect of the mechanism of action of a microemulsion oil-displacing system is the phase distribution of its surface active components in the oil – microemulsion composition – reservoir water system. It is experimentally found that the closeness to one of surfactant distribution coefficient is a required condition of the super-low inter-phase tension, phase inversion, and the formation of mid-phase microemulsions. In mid-phase or critical microemulsions that are a type III systems according to Winzor's classification, there is the third, microemulsion (mid-

phase), rich with surfactants, that is found in equilibrium with the aqueous phase.

This type of systems is of interest, as it is optimum to recover the residual capillary-retained drip and film oil. The best system is regarded to be one, in which the mid-phase rich with rich surfactants solubilises the same amounts of oil and water and is characterized by ultra-low tension both on the borderline with the oil and water phases. Multifunctional surfactants or surfactant mixtures that have the same affinity to oil and water correspond to conditions of the existence of type III systems according to Winzor's classification. Therefore factors that have an effect on surfactant distribution between oil and reservoir water also determine the type of the phase diagram of the system. As a rule, industrial surfactants are mixtures of different molecules and oligomers that may be differently distributed between phases. This results in the sensibility of efficient hydrophilic-lipophilic balance (HLB) of surfactant systems to changes in their composition because of surfactant dilution or sorption during reservoir filtration. In this regard, there are continuing attempts within colloid-chemical concepts, in particular, proceeding from HLB concept, to formulate a number of requirements that, as expected, would be efficient in oil-displacing mid-phase microemulsion systems. In the first place, surfactants should be oil- and water soluble, form micelles both in aqueous and oil phases in order for them to solubilise both oil and water. Herewith, for surfactant distribution coefficient to be close to one and thereby the minimum interfacial tension would be achieved, the proximity of critical micelle concentration (CMC) values of surfactants in the water and oil phases is required. Furthermore, the energies of the intermolecular interaction of surfactants with water and oil should be large enough and close to each other. This condition is provided by a combination of strong hydrophilic and oleophilic groups in surfactant molecules. As demonstrated by experiments, to reach ultra-low interfacial tension and the formation of medium phase microemulsions, certain ion composition and ionic strength of both the system and formation water are important [37, 38]. In the thermodynamic interpretation, the function of additives of electrolytes and nonelectrolytes is to align CMC values in both

phases and reduce the energy of transfer of surfactant molecules between the phases.

Microemulsion compositions demonstrate high oil-displacing ability in laboratory research. However, all known field tests show their insufficient stability under reservoir conditions. This is due to the fact that resulting from various intraformational processes, *i.e.* hydrodynamic dispersion, sorption, chemical interaction with the rock and reservoir water, system composition quickly goes out of very narrow ranges of the optimum salinity and the ratio of solubilised water and oil volumes, wherein ultra-low interphase tension is present. Therefore the main efforts of researchers are currently aimed at expanding the range of these parameters and giving the ability to auto-adjust them to the systems.

To elaborate these systems, there are attracted the theory and practice of phase transformations in liquid – liquid systems near the critical state that is characterised by super-low interphase tension. Many researchers in the area of colloid chemistry have long noted the relationship of stability problems of lyophilic nanodisperse systems and lyophilic colloids with the problem of critical states and second-order phase transitions. For explorers involved in the task of enhanced oil recovery, the attractiveness of this problem is primarily due to the opportunity of practical implementation of the critical state, or rather, the area of critical states as medium phase microemulsions or micellar solutions characterized by ultra-low interphase tension both in the borderline with oil and water, and having enhanced oil-displacing ability. Nowadays an approach to the creation of such liquids is being formed proceeding from ideas about the critical state [37, 38].

It is known that the critical state is a special point in the phase diagram, wherein the difference between the coexisting phases disappears and the interfacial tension becomes zero. To take only three-phase systems, then according to the phase rule, a single component system has no critical points, a two-component system has one critical point, a three-component system has a set of critical points, that is, the critical state is easier to implement and it would be more stable in a multi-component system. This is the main conclusion of practical importance. Another output no less important, lies in the fact that the interfacial tension may

go to zero even before the coexisting phases become identical in composition, *i.e.* near the critical state. From the standpoint of thermodynamics, interfacial tension is the free energy of an interfacial surface, which is the difference between the internal energy of the surface and the multiplication of temperature on the entropy of this surface. Therefore in order for the interfacial tension to approach zero, it is not necessary that the internal energy and entropy become equal to zero, it is enough that their difference tends to zero. This condition corresponds to the region of states near the critical one, where the difference between contacting phases disappears at the macro level, in other words, the macroscopic surface of the phase section becomes unstable and the phases spontaneously disperse. The system becomes nano-heterogeneous and an additional degree of freedom appears in it due to this. Such a nano-heterogeneous system, in particular, mid-phase microemulsion one, would be thermodynamically stable, as the cost of free surface energy for spontaneous dispersion of the macrophase is compensated by the gain of free energy due to an increase in entropy due to the inclusion of isolated microemulsion drops in thermal (Brownian) motion. According to J. I. Frankel [40], the enhanced entropy occurs due to a special form of surface thermal motion that can be considered as a result of a superposition of capillary waves. In this sense, the formation of microemulsion with ultra-low interfacial tension is due to the fact that capillary waves describing the surface thermal motion and causes the entropy term in the expression for the interfacial tension, lose their value at a sufficiently small value of the surface even long before the latter reaches molecular dimensions during dispersing one liquid in another partially miscible with it. Capillary waves penetrate deep into the liquid at a distance of the order of the wavelength, that is, they exist on the surface of the droplet only as long as the linear size of the droplet is much greater than the wavelength. Of course, capillary waves disappear, when the droplet size becomes smaller than their wavelength.

J. I. Frankel's points of view are in tune with modern ideas, for example, those developed by de Gennes [41] and are useful for working in the field of microemulsions for enhanced oil recovery. Practically important, are the fol-

lowing theoretical aspects: the key role of disordered (amorphous) surface phases in the formation of microemulsion; the flexible bicontinuous boundary as the surface of the eutectic; co-surfactants as a disordering component in microemulsions. Microemulsions with ultra-low interphase tension and high viscosity that solubilise oil and water are promising as oil-displacing fluids for enhanced oil recovery of heavy oil pools.

CHEMICALLY EVOLVING SYSTEMS FOR ENHANCED OIL RECOVERY

The current trend in the development of physicochemical EOR methods is based on smart materials with a complex hierarchical structure [42–45]. The development of systems that chemically evolve directly in the reservoir, with the acquired physicochemical properties, optimum for oil displacement purposes, is promising. Gels and sols, oil-displacing liquids with a high acid-base buffer capacity, emulsion and gas – liquid systems of colloidal degree of dispersion are generated resulting from the chemical evolution of the systems [44–48].

Chemically evolving systems including composition, able to chemically react with the reservoir rock and reservoir fluids, such as those that change their composition and properties during moving in the reservoir, change its composition and properties, in particular, being initially acid rock-dissolving ones, after the interaction with the rock become neutral or alkaline oil-displacing system and sol-forming systems are promising for pools with hard-to-recover oil and gas reserves in hydrophobic productive reservoirs with low permeabilities.

Oil-displacing systems based on surfactant and alkaline buffer system

For a number of years, the IPC SB RAS has been developing the concept of impact for the high-viscosity oil pool by surfactant-based systems that chemically evolve in the reservoir under the action of the heat-carrier forming CO₂ and ammonia buffer system [6, 22, 27–29, 49–52]. Prior to steam injection, the fringe of the composition based on the surfactant – carbamide – salt ammonium – water system is pumped into the well. The carbamide in the reservoir is hydrolyzed under the action of

high temperature to form carbon dioxide and ammonia. Unlike ammonia, carbon dioxide is much more soluble in oil than in water. The distribution coefficient of CO₂ in the oil – water system in the range of temperatures of 35–100 °C and pressures of 10–40 MPa is found within 4–10, while for ammonia it is not higher than $6 \cdot 10^{-4}$. Therefore the oil phase in the oil – water system would be enriched with CO₂; the aqueous one – with ammonia forming with an ammonium salt an alkaline system in the maximum buffer capacity in the pH 9–10 range, optimum for oil displacement purposes [6, 49–52]. Herewith, there are several useful effects. The dissolution of CO₂ in oil results in decreasing its viscosity. Carbon dioxide and ammonia in vapour phase facilitate the preservation of a vapour-gas mixture at a temperature below vapour condensation temperature and enhance transfer process efficiency of oil components by the distillation mechanism. The former reduce swelling clay minerals of the reservoir rock and thereby contribute to the preservation of the initial permeability of the reservoir. The ammonia buffer system formed during NH₃ dissolution in an aqueous solution of ammonium salts performs the same function. In addition, due to its alkalinity, pH 9–10, and the presence of surfactants, it contributes to the intensification of counter-current impregnation and additional oil displacement, a reduction in interfacial tension and destructuring, liquefaction of high-viscosity layers or films at the oil-water-rock boundaries that worsen the filtration of liquids in the reservoir and reduce the completeness of oil recovery [49–52]. Surfactant-based oil-displacing systems that generate CO₂ in the reservoir under TSS and alkaline buffer system (NINKA[®] systems) and facilitate decreasing viscosity of oil and its additional displacement were developed on the ground of performed research.

The field test of NINKA[®] systems was carried out in Permian-Carboniferous deposit of Usinsk field and Goshen deposit (China) in 2003–2007. It is found that their use during stationary vapour injection results in decreased water cut by 10–20 % and enhanced oil production rate on average by 40 %. During CSS, there are enhanced oil recovery by 1.5–3 times

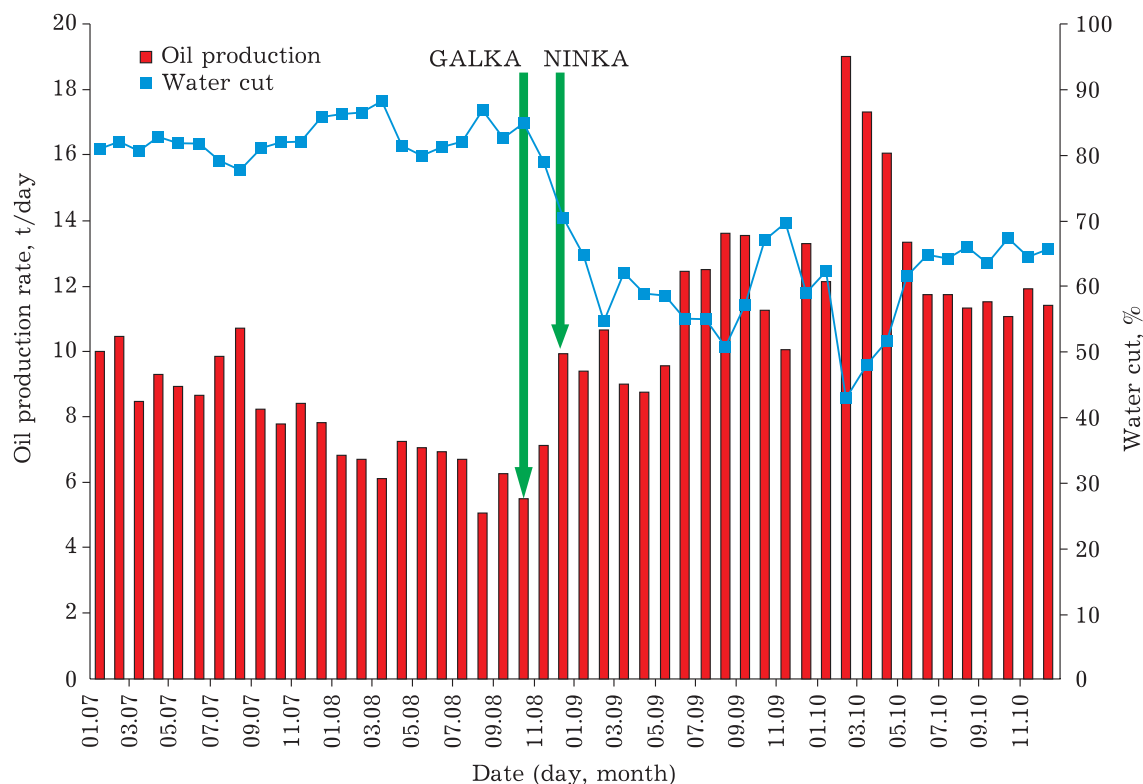


Fig. 4. Oil production increase for No 6168 in Permian-Carboniferous deposit of Usinsk field after injection of GALKA[®] and NINKA[®] systems.

and decreased oil viscosity by 2–3 times. Currently, technologies using NINKA[®] systems are being used on an industrial scale.

The prospects of the complex technology of alternating vapour injection, thermotropic gel-forming and oil-displacing systems have been demonstrated. The technology is used on an industrial scale. In 2008–2011 after downloading GALKA[®] and NINKA[®] systems, into the 41th steam injection well of Usinsk oilfield, there was oil flow rate increase for the oil by 4–30 t/day, water cut decrease by 5–20 % (Fig. 4). In 2014–2016, there were successfully carried out the injections of these systems 82 into steam wells. The results of performed operations demonstrate the synergism of methods of thermal-stream and gas-chemical exposure stimulation on the reservoir, the prospects of their complex application to enhance oil recovery of high-viscosity oil pools.

The further development of research was the development of systems with adjustable viscosity and alkalinity that increase both oil displacement efficiency and reservoir sweep efficiency during flooding and TSS. There has

been developed a thickened oil-displacing system based on surfactants, ammonium salts, aluminium, and carbamide (NINKA-Z) that simultaneously becomes flow-deflecting and oil-displacing one resulting from chemical evolution directly in the reservoir [31, 44]. Carbamide is hydrolyzed therein forming CO₂ and NH₃ that yields an alkaline ammonium buffer system with ammonium salts optimum for oil displacement purposes. Increasing pH causes ammonium salt hydrolysis to form aluminium hydroxide sol. Herewith, system viscosity increases by 1–2 orders. This results in increasing reservoir coverage by heat exposure, the involvement of low-permeable sublayers, reduction of viscosity of oil and its additional washing out. Resulting from this, there is an increase in sweep efficiency coefficient, oil recovery factor (ORF) and intensification of its recovery.

As demonstrated by research on the kinetics of sol formation and rheological properties of solutions and sols obtained at 90, 150, and 200 °C, after thermostating solutions of a sol-forming oil-displacing composition with ad-

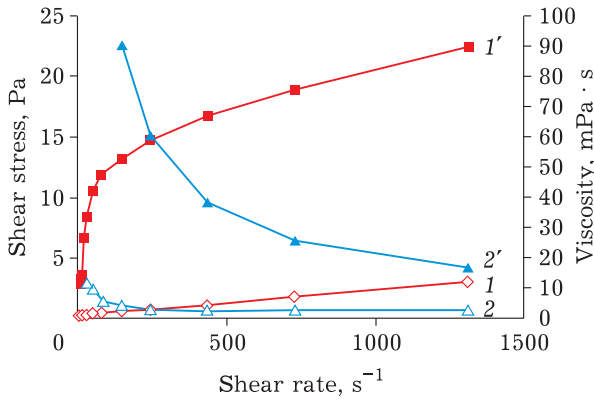


Fig. 5. Rheological curves of the flow (1,1') and viscosity (2, 2') of a solution of the NINKA-Z sol-forming oil-displacing system before (1, 2) and after 5 hrs of thermostating at 150 °C (1', 2').

justable viscosity and alkalinity depending on the concentration of aluminium salt, the viscosity of system solutions increases by 6–78 times, their pH after thermostating increases to 7.7–10 pH units.

As an example, Fig. 5 gives exploration results of rheological properties of solution com-

position (aluminium salt concentration of 2.5 %) before and after sol formation resulting from thermostating at 150 °C for 5 hrs. The measurements were carried out after cooling the solution to 20 °C. As can be seen from the figure, the system is a Newtonian liquid before thermostating and a viscoplastic liquid after sol formation (Fig. 5).

The field test of the system and injection of thickened NINKA-Z system into 7 steam wells in the TSS area in Permian-Carboniferous deposit of Usinsk field, Komi Republic were carried out in 2014–2015 (Fig. 6). The volume of injection was 80–110 m^3 per well; the effect was monitored according to 75 producing wells of the site. According to the results presented in Fig. 6, a steady water cut decrease and enhanced oil recovery after injection take place. The total effect along the section was 70 thousand tons of additional oil produced.

Chemically evolving systems based on surfactants, coordinating solvents, and complex compounds

Chemically evolving systems are traditionally developed as acid systems, towards com-

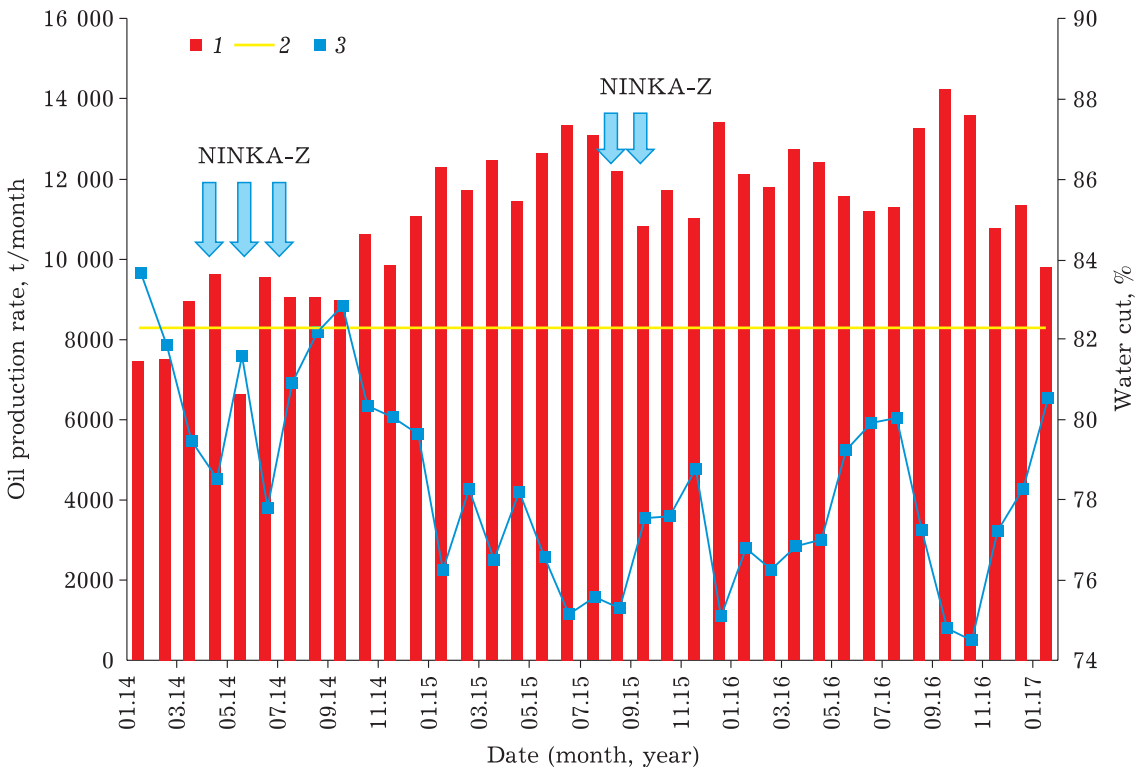


Fig. 6. Oil production increase and water cut decrease before and after injection of the NINKA-Z system into steam injection wells in 2014–2015. 1 – oil production rate, 2 – average oil production rate before treatment, 3 – water cut.

plication of their composition with broadening a range of useful functions. Alongside with known acids, complex acids formed as a result of donor-acceptor interaction of system components begin to be used. The composition and properties of complex acids are regulated by concentrations and donor/acceptor ratio. Complex acids have surface-active properties and may simultaneously increase the oil recovery of low-permeable reservoir matrix at the same time due to dissolution and capillary counter-current matrix impregnation. Boratofluoric acid-based systems may be an example of the practical use of complex acids in enhanced oil recovery technologies [53].

The IPC SB RAS explores the chemically evolving system as surfactant systems based on inorganic polybasic acids, such as boric and phosphorus, and coordinating solvents, *i.e.*, polyatomic alcohols (polyols) [54–58]. Complex acids that are much stronger than the initial acid are formed in inorganic acid/polyol systems due to donor-acceptor interaction. It makes it possible to enhance the acidities of oil-displacing systems and increase the duration of their action in the reservoir due to increased buffer capacity and extended buffer action range in the acid region of pH. Donor-acceptor interaction proceeds in a medium of an aqueous solution of a polyol such as glycerol, mannitol, and sorbitol.

This solution is a coordinating solvent and the polyol therein is a Lewis base, electron pair donor. Lewis acids, *i.e.* boric and phosphorus ones dissolved in a coordinating solvent, and also some metal aqua ions, such as calcium, magnesium, and aluminium, are acceptors of donor electron pair. A chemical bond of donor-acceptor type has properties of a polarized covalent bond and is called coordinate or dative bonding. Donor-acceptor interaction results in generating a molecular donor-acceptor complex referred to as a coordination compound or an adduct. The complex is a much stronger acid than the initial Lewis acid. In Russia and abroad, this fact has attracted interest towards

to the exploration of an opportunity to use complex acids in physicochemical technologies of enhanced oil recovery.

Figure 7 gives a scheme for the formation of a complex acid and its dissociation on an example of boric acid and glycerol.

The oxygen atom in the glycerol molecule is a donor giving its lone pair of electrons onto a vacant orbital of the acceptor that is the boron atom in the boric acid species. Resulting from this, a molecule of a coordination compound, *i.e.* glycerol boric acid that is four orders of magnitude stronger than boric acid is formed from one boric acid species. Instead of boric acid in this scheme, there may be metal aqua ions which have properties of a Lewis acid, for example, doubly charged cations of calcium and magnesium or triply charged ones of aluminium and iron. Molecules of complex acids are able to interact with metal aqua ions due to their alcohol hydroxyl groups. Figure 8 gives a reaction scheme, wherein the stereochemical feature of the glycerol boric acid molecule that is its ability to form soluble external cyclic complexes with metal ions due to the terminal hydroxyl groups.

During increasing the concentrations of metal aqua ions in a solution, alongside with cyclic structures, generating polymer-like associates, wherein metal aqua ions act as bridges binding molecules of the complex acid into linear and branched associative structures is probable. This cross-linking usually leads to substantial viscosity increase. The method for control of viscosity and density by additives of the indicated metals may be useful to regulate physicochemical and rheological properties of systems. In addition, this interaction facilitates the compatibility of complex acids based on polyols with reservoir water, particularly, with highly mineralized ones with large contents of calcium and magnesium salts.

The boric acid – polyol – electrolytes – water system is of interest as the basis of a new type of oil-displacing liquids that are effective at reservoir temperatures, whereby traditional oil-displacing liquors are ineffective. Physico-

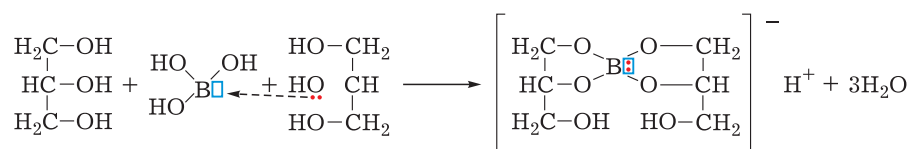


Fig. 7. Donor-acceptor interaction of boric acid and glycerol to form glycerol boric acid.

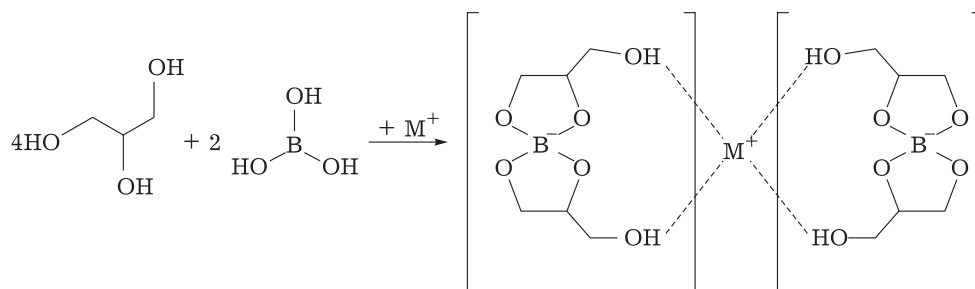


Fig. 8. Scheme for interaction of glycerol boric acid with metal cations in a solution to form soluble outer-sphere cyclic complexes.

chemical properties of this system are driven by the donor-acceptor interaction of polyatomic alcohols with boric acid, in which anions of the acid act as a four-component ligand, which is a Lewis acid. Resulting from this, depending on the pH and the nature of the electrolytes present, various coordination complexes of glycerol and boric acid anions are generated in this system. During the interaction with water-soluble non-ionic surfactants, these complexes form effective oil-displacing fluids with high wetting and washing ability.

As demonstrated by experimental research of acid-base equilibria in boric acid – polyol – water systems carried out in the IPC SB RAS, during the interaction of boric acid and polyols resulting from the formation of complex acids in the pH value of 1% boric acid solution in aqueous alcohol solvents decreases from 5.9 pH to 1.7–2.7 pH units, 5% solution – from 3.4 to 1.5–2.2 pH units and 10% to pH 1.3–1.8 pH units with an increase in the concentration of polyols in the solvent. Herewith, decreasing the pH with increasing polyol concentration is of monotonic nature, which is driven by a continuous shift of ionization reaction equilibrium conjugated with shifting the reaction of the formation of boric acid and polyol, which is confirmed by the computed values of concentration constants of formation and ionization of glycerol boric acid in glycerol coordinating solvents.

Resulting from investigating the effect of electrolytes on acid-base equilibria of solutions in the water – glycerol – boric acid system, it is found that metal chlorides, such as AlCl₃, FeCl₃, FeCl₂ and MgCl₂ have the strongest effect on the acid equilibrium (Fig. 9). For example, during increasing the concentration of aluminium chloride in a solution to 20 mass %, pH values decrease to –0.54 pH units, while

magnitudes of viscosities of solutions increase to 17500 mPa · s.

On the basis of research in IPC SB RAS, an acid oil-displacing system of the prolonged action based on the adduct of boric acid and glycerol (the glycerol boric acid system) that implements the concept of chemically evolving systems has been developed. The system is compatible with mineralized reservoir water and has a low freezing point (–20...–60 °C) and low interfacial tension in the boundary with oil. The system is applicable for enhanced oil recovery and oil production intensification due to increasing the permeability of reservoir rocks and the productivity of producing wells in a broad temperature range, from 10 to 250 °C.

It is most effective in carbonate reservoirs, in particular, Permian-Carboniferous deposit of Usinsk field. The system has a delayed reaction with carbonate rocks. High oil-displacing ability, compatibility with mineralized reservoir water, and decrease in the swelling of clays lead to the additional washing of residual

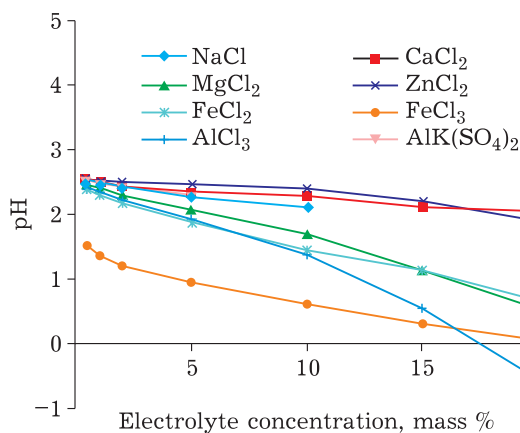


Fig. 9. Effect of electrolytes on the acid equilibrium in the boric acid – water – glycerol system at 20 °C.

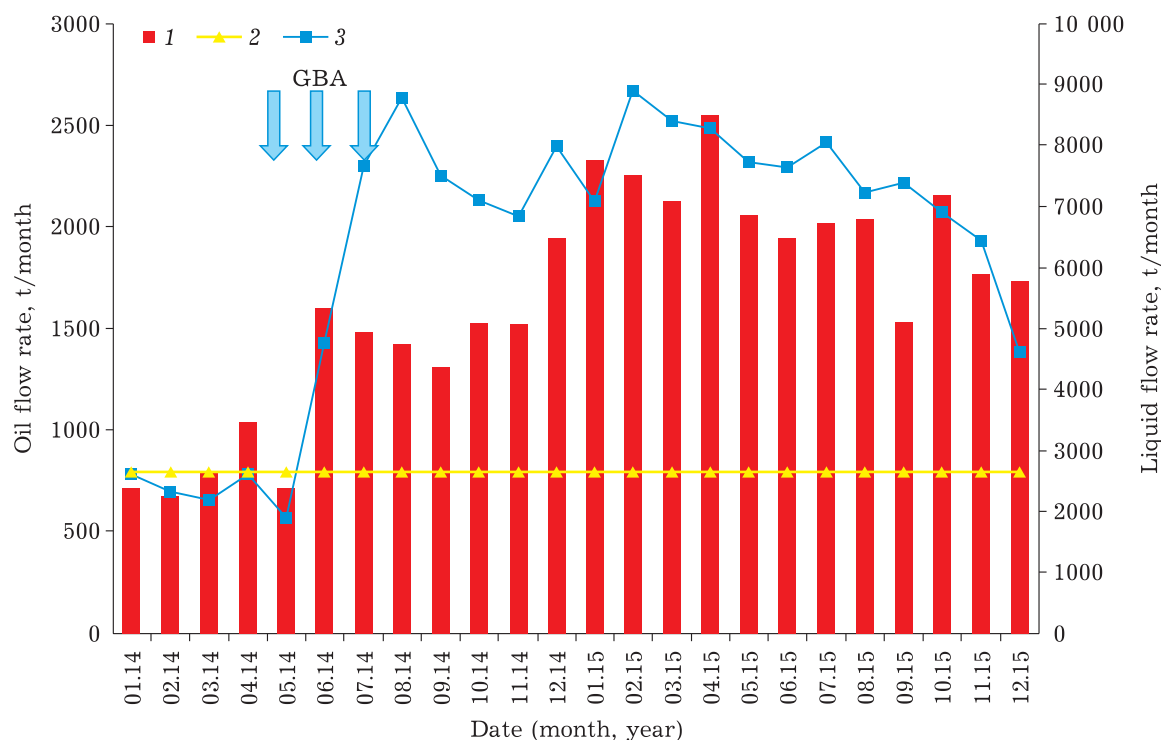


Fig. 10. Results of use of the glycerol boric acid system in total for 10 low producing wells in Permian-Carboniferous deposit of Usinsk field: the effect continues for 19 months, additional oil production of ~20,000 t, or 2,000 t/well. 1 – oil flow rate, t/month, 2 – average for 2014 before treatment, 3 – liquid flow rate, t/month.

oil from both high- and low-permeable zones of the formation.

Resulting from the interaction of the system with the carbonate reservoir, CO_2 is released and dissolves in oil and reduces its viscosity, which contributes to an increased degree of oil production. In addition, resulting from the interaction with the carbonate reservoir and hydrolysis of carbamide that is a part of the system, its pH increases from 2.8–3.1 to 8.8–10.0 and it chemically evolves, turning into an alkaline oil-displacing system that ensures efficient oil displacement and the prolonged impact on the reservoir. After thermostating with the glycerol boric acid system and carbonate reservoir at a temperature of 70–120 °C, oil viscosity is reduced by 1.2–2.7 times.

Systems based on surfactants that coordinate solvents and complex compounds have demonstrated high efficiency under field conditions (Fig. 10) and are recommended for the commercial introduction. It is worth noting high processibility of these systems, as only standard oil field equipment is used for their preparation and injection.

Oil-displacing systems based on complex acids are environmentally friendly and provided with raw material resources. It is sufficient to note that the world production of crude glycerol as a side product of the industrial synthesis of biodiesel fuel was about 40 million tons in 2016. Moreover, for purposes of enhanced oil recovery, it is not required to refine and purify raw glycerol from impurities, which significantly reduces its cost and makes the technologies cost-effective.

CONCLUSION

To intensify the development and enhance oil recovery for fields with hard to recover reserves including heavy high-viscosity oil pools, physicochemical methods of enhanced oil recovery built on nanoheterogeneous chemically evolving systems based on surfactants, both as cold technologies and together with TSS, appear to be promising.

Large-scale industrial applications of the new technologies would allow prolonging revenue producing service of deposits at the late

stage of development and facilitating the promotion of oil producing industry and the expansion of its fuel and energy sector.

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