Review of the Scientific Advisor

for the dissertation Thesis submitted on the Requirements for the Degree of Doctor of Philosophy (Ph.D.) in the specialty 6D073900 - "Petrochemistry" at Satbayev University, Almaty, Republic of Kazakhstan

by Nurbatyr Mukhametgazy

entitled "Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications"

The submitted Ph.D. dissertation of Nurbatyr Mukhametgazy entitled "Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications" describes the fundamental aspects of acrylamide-based polyampholytes that potentially might be applied in enhanced oil recovery (EOR), as water based drilling fluids (WBDFs), and as tracer agent for monitoring of interwell connections between injection and production wells.

The ability of amphoteric polyelectrolytes to swell and be effective viscosity enhancers in high salinity and high-temperature reservoirs plays a crucial role in enhanced oil recovery (EOR) processes. Strongly charged (or quenched) polyampholytes due to salt- and temperature resistance can serve as viscosifying agents in EOR where thickeners are required in brine solution. In this regard, amphoteric polyelectrolytes – polymers which have both positively and negatively charged monomers, are promising, because in high saline water the anions and cations of salts screen the electrostatic attraction between positively and negatively charged groups of the polymer chain and increases the viscosity of the brine solution.

The present Thesis is devoted to synthesis and characterization of specially designed polyampholyte terpolymers based on nonionic monomer – acrylamide (AAm), anionic monomer – 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and cationic monomer – (3-acrylamidopropyl) trimethylammonium chloride (APTAC) for application in EOR, which proves the relevance of this research.

With increasing global energy consumption, oil/gas drilling technology considerably expanded from conventional reservoirs to deep and ultra-deep reservoirs. However harsh geological conditions including high temperature and high salinity require thermo- and salt tolerant water-based drilling fluids (WBDF). Conventional polymer additives, such as hydrolyzed poly(acrylamide) (HPAM), polyanionic cellulose and carboxymethyl (or ethyl) cellulose work badly in saline environment due to the polyelectrolyte effect. Expanded (or swollen) in pure water polyelectrolyte chains shrink in salt solution due to the screened electrostatic repulsion between uniformly charged macroions (polyelectrolyte effect) and adopt coil conformation. In its turn this leads to worse keeping the hydration dispersion becoming poorer in performance and even to insolubility. To overcome this problem in this Thesis the WBDF containing salt-tolerant polyampholyte AAm-AMPS-APTAC, bentonite and various functional additives was developed for the wells with high salinity.

In the frame of this Thesis the trace amount of fluorescent monomer – acrylamide Nile Blue (1 mol.%) was introduced into the composition of previously developed quenched polyampholyte AMPS-APTAC to prepare globular and fully electroneutral macromolecular chains to minimize or even exclude its adsorption to the rock and clay materials. The

advantage of proposed approach is that the quenched polyampholyte of equimolar composition containing fluorescent dye – Nile Blue is insoluble in oil, but water-soluble, salt tolerant, detectable in very low concentrations, and does not adsorb on the rock or clay minerals. In the present Thesis the passing of fluorescently-labeled ternary polyampholyte based on acrylamide derivatives through the core sample was demonstrated for monitoring of well-to-well connections.

Thus, the relevance of the present Thesis is to develop temperature- and salt-resistant polyampholytes for oil industry of Kazakhstan

The novelty of the PhD Thesis of Nurbatyr Mukhametgazy is that the high molecular weight ternary polyampholytes based on AAm-AMPS-APTAC were synthesized for the first time and they have a superior oil displacement capability in high-saline reservoirs compared to hydrolyzed polyacrylamide (HPAM) traditionally used in EOR. An increase in the viscosity of ternary polyampholytes in brine solution is due to disruption of intra- and interionic contacts between the oppositely charged AMPS and APTAC moieties, leading to unfolding and expansion of macromolecular chains (*antipolyelectrolyte effect*). The injection of 0.25% amphoteric terpolymer and HPAM solutions prepared in 200 g/L brine into the 0.62 and 1.77 Darcy sand packs resulted in the increase of the oil recovery factor by 28 and 18%, respectively. Incremental 10% oil recovery by AAm-AMPS-APTAC confirms that the amphoteric terpolymer has a higher oil displacement capacity than HPAM.

Moreover, the salt-tolerant ternary polyampholyte AAm-AMPS-APTAC was applied for preparation of water-based drilling fluid. The novel amphoteric terpolymer possessed not only to boost its salt tolerance but also to enhance drilling mud performance (viscosity and filtration properties) under lower temperature geothermal conditions.

For the first time the trace amount of fluorescent monomer – acrylamide Nile Blue (ANB) was introduced into the composition of AMPS-APTAC copolymer. As a result, the novel ternary polyampholyte [AMPS]:[APTAC]:[ANB] = 50:49:1 mol.% with globular structure and fully electroneutral macromolecular chains to minimize or exclude its adsorption to the rock was obtained. It was characterized by physico-chemical methods and core flooding tests as tracer agent for fluorescence-detection technology in oil industry for monitoring of well-to-well connections.

Personal contribution of Nurbatyr Mukhametgazy is demonstrated by the collection, analysis, and summarization of the available literature on polyampholytes, performing experiments, and interpreting and discussing the results.

Results of the research work are reflected in 12 publications: 1 article – in the Scientific Journal cited in the Scopus base (Q1, 77 percentile), 1 article in AIP Conference Proceedings (Q4, 17 percentile), 4 articles – in the Scientific Journals listed in the recommended by the Committee for Quality Assurance in the Sphere of Education and Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan, and 1 publication in other scientific journals and publications (Kazakhstan Journal for the Oil & Gas Industry). Scientific results were also reported at 5 International Conferences and Symposiums.

The dissertation is composed of six chapters. The introduction presents the general overview, relevance, objectives, hypotheses, and dissertation organization. Chapter I provides the literature survey on polyampholytes, especially in relation to petroleum industry. Chapter II is describes the experimental part, including materials, methods and used instruments, Chapter III is devoted to synthesis and characterization of polyampholytes and reological study, Chapter IV presents results of core/sand pack flooding

experiments with polyampholyte terpolymers and hydrolyzed polyacrylamide aqueous solutions, Chapter V describes the preparation protocol of drilling fluids, Chapter VI considers the synthesis and characterization of fluorescently labeled polyampholyte as well as core flooding experiments, Chapter VII is conclusions. The total volume consists of 113 pages, including 67 figures, 14 tables and references of 206 titles.

In conclusion, by its relevance, the scientific and practical value dissertation work of Nurbatyr Mukhametgazy entitled "Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications" corresponds to the requirements of the Committee for Supervision and Certification in Education and Science of the Ministry of Science and Higher Education. Therefore, the dissertation author deserves the Doctor of Philosophy (Ph.D.) in the specialty 6D073900-Petrochemistry.

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