На основе акриламида негізіндегі поліамфолит синтезі және сипаттамасы

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Синтез и исследование нового тройного полиамфолита на основе акриламида в качестве трассерного агента

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Только заряженный жана уштіқ куәлымды полиамфолит, аниондық мономер — 2-акриламидо-2-метил-1-пропансульфоніфін қышқылы нейтрал түзу (АМПС), катиондық мономер — (3-акриламидопропил) триметиламмоний хлорид (АПТМАХ) және оң зарядалған флуоресцентті белгі — акриламид Нил голубой (АНГ) бос радикалды сополимерлену өзінен синтезделді және ол ИК-Фурье светорассеяние, ультракүлгін-көрініс, динамикалық шашырау және дзета потенциалды арқылы сипатталды.

Новый тройной полиамфолит, состоящий из сильно заряженного анионного monomer–нитриевой соли 2-акриламидо-2-метил-1-пропансульфоновой кислоты (АМПС), катионного monomer—(3-акриламидопропил) триметиламмоний хлорида (АПТМАХ) и положительно заряженного флуоресцентного красителя – акриламид Нил голубой (АНГ) синтезирован методом свободнорадикальной сополимеризации и он характеризован методами ИК-Фурье, УФ видимой и флуоресцентной спектроскопии, динамического светодиогоения и дзета-потенциала.

Тоқыл іздеуші агент ретіндегі трассер. Флуоресцентті белгісі бар үштік полиамфолит ұңғымалар арасындағы флуоресценттік спектрограмма анық, көздөр мен сәулелену шыңдары, терполимердің AНГ топтарына жатады. AMПСҚ-АПТМАХ-АНГ анық, AНГ топтарының сәйкесінше 4,3 нм және ξ ≈ −1,6 мВ, тоқылған қышқылы және үлгісіне 0,1% (1,3⋅10^−3 моль⋅л^−1) AMПСҚ-АПТМАХ-АНГ ерітіндісін айдау кезінде флуоресцентті белгісі бос радикалды сополимерден керн арқылы тау жынысына адсорбциясыз. Флуоресцентті белгісі бар үштік полиамфолит ұңғымалар арасындағы флуоресценттік спектрограмма анық, көздөр мен сәулелену шыңдары, терполимердің AНГ топтарына жатады. AMПСҚ-АПТМАХ-АНГ анық, AНГ топтарының сәйкесінше 4,3 нм және ξ ≈ −1,6 мВ, тоқылған қышқылы және үлгісіне 0,1% (1,3⋅10^−3 моль⋅л^−1) AMПСҚ-АПТМАХ-АНГ ерітіндісін айдау кезінде флуоресцентті белгісі бос радикалды сополимерден керн арқылы тау жынысына адсорбциясыз.

Ключевые слова: полиамфолитный тройной сополимер; синтез; характеристики; заводнение керна; фильтрация; трассер.
Synthesis and characterization of novel acrylamide-based ternary polyampholyte as tracer agent

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(This paper is dedicated to 70th anniversary of Professor Sarkyt E. Kudaibergenov)

1. Introduction

The strongly charged or “quenched” polyampholyte (QPA) represents a macromolecule consisting of static positive and negative charges independently on pH [1-3]. Earlier [4-7] we have considered the behavior of linear and crosslinked QPA based on fully charged anionic monomer – 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and cationic monomer – (3-acrylamidopropyl) trimethylammonium chloride (APTAC) in aqueous-salt solutions, complexation ability with respect to ionic dyes, surfactants, swelling and mechanical properties. Later on [8,9] we have reported the applicability of amphoteric terpolymers composed of AMPS, APTAC and acrylamide (AAM) as viscosifying agent in enhanced oil recovery (EOR). Equimolar QPA based on AMPS-APTAC dissolved in saline water with mineralization more than 200 g.L⁻¹ was also tested to evaluate the flow behavior through porous media [10]. It was found that AMPS-APTAC solution is able to pass through the porous media model. This invoked us to synthesize equimolar QPA composed of equal numbers of anionic and cationic monomers containing also a small amount of fluorescent monomer – acrylamide Nile Blue for application as an interwell tracer agent. The main reason of selection of ternary copolymer AMPS-APTAC-ANB as polymeric tracer is that it is water-soluble, highly stable thermally, chemically, physically, and biologically in oil reservoir conditions, salt tolerant in oilfield water, detectable in very low concentrations, low toxic, and has minimal adsorption to the rock [11]. In the present communication we demonstrate that the transport behavior of ternary copolymer AMPS-APTAC-ANB through the core can open new smart tracing possibilities for monitoring well-to-well connections.

2. Experiment

2.1. Materials

2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS, 98 wt.% in water) and (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75 wt.% in water), acrylamide Nile Blue (ANB, dark blue crystals, purity 99%) and ammonium persulfate (APS, purity 99%) were purchased from Sigma-Aldrich Chemical Co. and used without further purification. The core sample of 3.9 cm length and 2.95 cm diameter purchased from “Vostochnyi Moldabek” oilfield #2524 from the depth of ≈ 500 m has the porosity of 0.094% and permeability of 1 mD. According to elemental analysis the core sample mostly consists of aluminosilicates of calcium, iron and potassium. Brine solution from “Vostochnyi Moldabek” oilfield #2524 with mineralization 100 g∙L⁻¹ was used for core flooding test.

2.2. Methods

Absorption, fluorescence and FT-IR spectra of AMPS-APTAC-ANB were registered on UV-Vis spectrophotometer (Specord 210 plus BU, Germany), F97 Pro fluorescence spectrophotometer (China) and Carry 660 (Agilent, USA), respectively. The fluorescence spectrum of AMPS-APTAC-ANB was recorded at emission wavelength λₘₐₓ = 660-680 nm that is very close to emission spectrum of monomeric ANB in water (λₘₐₓ = 674 nm). The average hydrodynamic size and ζ-potential of AMPS-APTAC-ANB were determined with the help of a dynamic light scattering (DLS) device (Malvern Zetasizer Nano ZS90, UK). The core flooding experiments were conducted with the help of special core flooding set up “УИК-С(2)” (Russia).
3. Results and Discussion

3.1. Synthesis and characterization of AMPS-APTAC-ANB terpolymer

Acrylamide-based ternary polyampholyte AMPS-APTAC-ANB was synthesized via conventional free radical (co) polymerization at the molar ratio of initial monomers [AMPS]:[APTAC]:[ANB] = 50:49:1 in the presence of APS at 60°C during 4 h (Figure 1).

Table 1 – Identification of FTIR spectrum of AMPS-APTAC-ANB

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>v(NH)</th>
<th>v(CH)</th>
<th>v(CONH) Amide I</th>
<th>v(CONH) Amide II</th>
<th>δ(CH₃)</th>
<th>v(S=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band assignments, cm⁻¹</td>
<td>3427</td>
<td>2938</td>
<td>1649</td>
<td>1550</td>
<td>1185</td>
<td>1040, 969</td>
</tr>
</tbody>
</table>

Figure 2 and Table 1 show the FTIR spectrum and characteristic bands of functional groups of AMPS-APTAC-ANB. FTIR spectra of AMPS-APTAC (50:50 mol.%) and AMPS-APTAC-ANB (50:49:1 mol.%) are identical, meaning that 1 mol.% of ANB in terpolymer composition does not influence the characteristic bands of polyampholytes [4]. UV-Vis spectra of AMPS-APTAC-ANB in aqueous solution exhibit well-defined absorption maximum at λ_{max} = 586 nm that is attributed to ANB group of terpolymer (Figure 3).

The average hydrodynamic size and zeta potential of AMPS-APTAC-ANB in aqueous solution are equal to 4.3 nm and ζ = −1.6 mV, respectively, that indicate on globular conformation of amphoteric macromolecules with slightly negative surface charge (Figure 4).

In pure water the AMPS-APTAC-ANB macromolecules are in globular state due to electrostatic attraction between oppositely charged monomer units. It is likely that the ANB molecules due to more hydrophobic character are replaced inside of globules as shown in Figure 5. It is expected that due to slightly negative surface charge of the AMPS-APTAC-ANB (ζ = −1.6 mV) its adsorption to negatively charged surface of core materials is minimal or even excluded.

3.2. Core flooding experiments with AMPS-APTAC-ANB solution

The fluorescence-detection technology attracts considerable interest in oilfield operations [11] due to many advantages over radioactive isotopes, ionic and organic tracers [12]. For evaluation of interwell permeability and porosity the authors [13] used fluorescent polycrylamide microspheres, which fluoresce under ultraviolet irradiation. A water-soluble...
Figure 3 – Visible spectra of AMPS-APTAC-ANB in aqueous solution (a) and calibration graph (b) plotted in coordinates “intensity-concentration” at concentration of [AMPS-APTAC-ANB] = 0 (1), 0.0625 (2), 0.125 (3), 0.25 (4), 0.5 (5) and 1.0 wt.% (6). Insert is a quartz cuvette containing aqueous solution of AMPS-APTAC-ANB.

Figure 4 – The average hydrodynamic diameter (a) and the value of zeta-potential (b) of 0.15 wt.% AMPS-APTAC-ANB in aqueous solution.

Figure 5 – Schematic representation of structural unit of amphoteric terpolymer AMPS-APTAC-ANB (a) and formation of globular structure (b) in dilute aqueous solution.
fluorescent polymer was prepared as a combination of a flooding agent and tracer by introducing a polymerizable rigid fluorescent coumarin monomer into polyacrylamide chains [14]. Fluorescent polymer microspheres were also obtained via the inverse suspension polymerization method with Rhodamine B as a fluorescence functional monomer [15]. As distinct from the abovementioned studies, in our case we have introduced a trace amount of fluorescent monomer acrylamide Nile Blue (ANB) into the composition of AMPS-APTAC quenched polyampholyte to prepare globular and fully electroneutral macromolecular chains to minimize or exclude their adsorption to the rock. The advantages of our approach are that the QPA of equimolar composition is water-soluble, salt tolerant and adopts globular and quasi-electroneutral conformation in aqueous solution due to mutual compensation of positive and negative charges. The core flooding experiments were conducted in the following sequence. At first, 40 mL of distilled water was injected into the core sample at 1 mL·min⁻¹. In the course of water injection, the pressure sharply increased during 5 min and leveled off at P = 0.08-0.10 MPa during 10-90 min. The effluents were slightly turbid due to washing out of fine dispersed microparticles present in the core sample. In the next stage 50 mL, 0.1 wt.% (or 1.3×10⁻³ mol·L⁻¹) aqueous solution of AMPS-APTAC-ANB were injected into the core sample preliminary washed out by distilled water (Figure 6). The injection rate of AMPS-APTAC-ANB was equal to 0.1 mL·min⁻¹. In the course of the test the injection pressure was increasing gradually and blue color appeared in the collected effluents.

Chase saline water flooding with salinity 100 g·L⁻¹ shows the linear increase in the pressure and replacement of residual amount of AMPS-APTAC-ANB entrapped within the core (Figure 7).

The presence of color initial 3 fractions of passed saline water confirm the replacement of AMPS-APTAC-ANB in core sample by saline water. The effluents were analyzed by UV-Vis at λ_max = 586 nm and fluorescence spectrophotometer at emission wavelength λ_max = 660-680 nm (λ_max of pure ANB in water is 674 nm) to determine the concentration of AMPS-APTAC-ANB passed through the core and displaced by saline water (Figure 8).

The fluorescence intensity of AMPS-APTAC-ANB gradually increases after injection of the first 6 mL of polyampholyte solution (Region 1). This is probably due to the dilution of polyampholyte by residual distilled water left in the core sample. A sharp increase in the fluorescence intensity is observed after injection of 7 mL of polyampholyte solution through the core. It means that the main portion of AMPS-APTAC-ANB passes through the core in Region 2. The fluorescence intensity of AMPS-APTAC-ANB levels off in Region 3 after injection of 12-25 mL of polyampholyte solution meaning that the core sample is fully saturated by fluorescently-labeled polyampholyte. Pumping of 100 g·L⁻¹ saline water into the core saturated by 0.1 wt.% AMPS-APTAC-ANB leads to the gradual decrease of the fluorescence intensity of polyampholyte solution. It is related to the replacement of AMPS-APTAC-ANB with saline water. After the injection of 28 mL saline water the fluorescence intensity of AMPS-APTAC-ANB decreases up to 38.5 a.u. It is 10 times lower than the initial concentration of...
Figure 7 – Time-dependent change of pressure upon injection of saline water from “Vostochnyi Moldabek” with salinity 100 g L\(^{-1}\) into the core sample after the injection of AMPS-APTAC-ANB (see Figure 6) and vials of collected effluents at T = 25 °C. The injection rate is 0.1 mL min\(^{-1}\).

AMPS-APTAC-ANB solution injected into the core (389 a.u.). This implies that AMPS-APTAC-ANB is replaced from the core sample by saline water. Thus, the novel QPA based on AMPS-APTAC-ANB may be promising tool for evaluation of interwell and interlayer connections, as well as heterogeneities of oil reservoirs.

4. Conclusion

A novel ternary polyampholyte consisting of 50 mol.% of anionic monomer – AMPS, 49 mol.% of cationic monomer – APTAC and 1 mol.% of cationic fluorescent dye – ANB was synthesized and characterized as oilfield tracer. Globular, electroneutral and nano-sized macromolecules of AMPS-APTAC-ANB in aqueous and aqueous-salt solution are proved to be able to pass through porous media. It is expected that the novel AMPS-APTAC-ANB formulation might be useful as a polymer tracer for monitoring of oil wells.

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References


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