Exploring of polyampholytes in EOR

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Abstract. Polyampholytes are unique macromolecules containing acid/base or anionic/cationic groups in the main or side chains that mimic the behavior of proteins, polypeptides and/or polynucleotides. Water-soluble and water-swelling polyampholytes exhibit salt-tolerant, thermalresistant, shear-stable, self-healing, anti-fouling, self-assembling, and stimuli-responsive properties that could have a broad impact in the areas of wastewater purification, desalination, enhanced oil recovery, stabilization of colloid dispersions, structural biomaterials, controlled drug delivery systems, energy and information storage devices, supercapacitors, actuators, and among others. This communication is devoted to the use of high-charged polyampholytes, hydrophobically modified polyampholytes, and oppositely charged polyelectrolyte complexes as effective viscosity enhancers in high salinity and high-temperature reservoirs for enhanced oil recovery. A comparative analysis is presented with hydrolyzed polyacrylamide, traditionally used in the oil industry. The discussion highlights the crucial role of the "antipolyelectrolyte effect" in brine solutions, emphasizing its significance in disrupting intraand interionic contacts between oppositely charged moieties, particularly in the context of oil recovery.

Introduction

Conditionally polyampholytes can be divided into 3 classes: annealed, quenched and betainic (or zwitterionic) [1-4]. Annealed polyampholytes consist of acid-base monomers that are ionized in dependence of pH, while quenched polyampholytes containing strongly charged cationic and anionic monomers retain their respective charges independently on pH. The "semi-annealed" or "semi-quenched" polyampholytes are defined as amphoteric macromolecules that combine the weak acid/cationic or weak base/anionic monomers. "Betainic" (or zwitterionic) polyampholytes are macromolecules containing identical numbers of acid-base (or fully charged anionic-cationic) species in the same monomer units [5, 6]. Examples of polyampholytes with different chemical structures are shown in Figure 1.



Figure 1. Repeating monomeric units of annealed (1), quenched (2), zwitterionic (3, 4), quenched betainic (5), annealed betainic (6) and self-annealed (or self-quenched) (7, 8) polyampholytes.

The behavior of polyelectrolytes, polyampholytes and interpolyelectrolyte complexes in saline water is demonstrated in Figure 2 [7].



Figure 2. Schematic illustration of the behavior of anionic and cationic polyelectrolytes (a, b), polyampholytes (c) and interpolyelectrolyte complexes (d) in aqueous-salt solution.

Expanded in pure water anionic and/or cationic polyelectrolyte chains shrink in salt solution due to the screened electrostatic repulsion between uniformly charged macroions (polyelectrolyte effect). Collapsed in aqueous solution "annealed" polyampholyte at the isoelectric point (IEP) and/or charge-balanced "quenched" polyampholyte, including interpolyelectrolyte complexes unfold in salt solution due to screening of the electrostatic attraction between oppositely charged monomers ("antipolyelectrolyte effect").

"Antipolyelectrolyte effect" of linear and crosslinked polyampholytes in saline water

One of the fascinating properties of polyampholytes is the so-called "antipolyelectrolyte effect" in aqueous solutions, predicted by Ehrlich and Doty [8], theoretically justified by Higgs and Joanny [9], and confirmed experimentally by many research groups [10-12] including this one [13-17].

The "antipolyelectrolyte effect" in contrast to "polyelectrolyte effect" is related to unfolding of amphoteric macromolecules at the isoelectric point (IEP) upon the addition of low-molecular-weight salts in contrast to salt-induced collapse of ordinary polyelectrolytes [18]. Recently [19] the antipolyelectrolyte behavior of polybetaine macromolecules was detected directly at the single-chain level. The "antipolyelectrolyte effect" was experimentally established by E.A. Bekturov and S.E. Kudaibergenov for annealed polyampholytes in 1979 [13] and by S.J. Candau et al. [20] for quenched polyampholyte gels in 1999 (Figures 3-5).







Figure 3. pH-dependence of the intrinsic viscosity of equimolar annealed polyampholyte in the presence of 0.005 (1), 0.01 (2), 0.1 (3), and 0.3M KBr (4).

Figure 4. 3D picture of equimolar annealed polyampholyte in coordinates intrinsic viscosity-pH-ionic strength redrawn from the data of Figure 3.

Figure 5. Evolution of swelling ratio at equilibrium Q_e as a function of the net charge fraction for MADQUAT-*co*-AMPS in pure water and 2 mol·L⁻¹ NaCl solution.

Polyampholytes in enhanced oil recovery (EOR)

To remove oil from nature, the presence of connate water represents one serious problem in oil recovery. The application of water-soluble polymers for enhanced oil recovery (EOR) is a challenging task for industries as well as academic research [21]. Synthetic and natural water-soluble and water-swelling polymers used for EOR should satisfy the following but not limited key requirements:

1. Regulation of the ratio of water mobility to oil mobility. Ideally, the mobility ratio is less than 1.

2. Viscosifying and/or mobility control agents in harsh conditions, i.e., high temperature and high salinity.

3. Reducing the oil/water interfacial tension (IFT).

4. Generating new types of emulsions for extraction of residual oil from nature oil reservoirs.

- 5. Long-term pH stability and resistivity to bacterial attacks.
- 6. Environmentally friendly. No hazardous effect on underground water.

The low-charge-density polyampholytes can be used as effective viscosity enhancers in high salinity and high-temperature reservoirs and be utilized in EOR processes [22-29]. Recently [30-34] a series of low-charge-density amphoteric terpolymers based on acrylamide (AAm), 2acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS), and (3acrylamidopropyl) trimethylammonium chloride (APTAC) were developed and their viscosifying ability with respect to reservoir saline water (200-300 g·L⁻¹) at 60 °C was evaluated. For polymer flooding experiments the appropriate salt tolerant sample [AAm]:[AMPS]:[APTAC] = 80:10:10 mol.% (abbreviated as AAm₈₀-AMPS₁₀-APTAC₁₀) was selected. The injection of 0.25 wt.% AAm₈₀-AMPS₁₀-APTAC₁₀ dissolved in 200 g·L⁻¹ brine resulted in a rise of incremental oil recovery factor (ORF) by 28 and 23% for the 0.62D and 1.8D sand pack models, respectively, in comparison with saline water flooding (Figure 6). The ORF between AAm-AMPS-APTAC and hydrolyzed polyacrylamide (HPAM) was compared, because the latter is the most studied and

traditionally used polymer in EOR (Figure 7). It is seen that the total mass of oil produced in the course of polyampholyte AAm_{80} -AMPS₁₀-APTAC₁₀ and HPAM injections is around of 28% and 18%, respectively, in comparison with the initial oil mass in the sand packs.





Figure 6. ORF for water and polymer flooding.

Figure 7. Comparison of ORF between AAm-AMPS-APTAC (1) and HPAM (2). The permeability of sand pack model is 0.62 Darcy.

This is explained by an increase in the viscosity of brine solution due to disruption of intra- and interionic contacts between the oppositely charged AMPS and APTAC moieties, demonstrating the "antipolyelectrolyte effect". This phenomenon leads to a decrease in the mobility factor (M), which is quantitative parameter of oil displacement with water:

$$M = \frac{k_w \cdot \mu_0}{k_0 \cdot \mu_w}$$

where *M* is mobility factor; k_w is water permeability; μ_0 is oil viscosity; k_0 is oil permeability; μ_w is water viscosity.

The hydrophobically modified polyampholytes (HMPA) may be effective viscosity enhancers in high salinity media and temperature as they combine the advantage of alkaline-surfactant-polymer (ASP) flooding [35-41]. Application of HMPA in EOR was reviewed in [42]. The viscosity of HMPA increases due to intermolecular association of hydrophobic parts [43]. Mixture of HMPA, C12/14 alkyl polyglycoside (APG1214), and n-alcohol was created and characterized by viscometry, oil/water interfacial tension (IFT) measurements, and checking the phase behavior [44] (Figure 8).



Figure 8. Structures of HMPA (a) and APG1214 (b).

Polyglycosides containing C12/14 alkyl groups (APG1214) were used as surfactants, with nalcohol as a co-solvent, to create as a physical linker between the oleic phase and the APG1214 monolayer for tuning the hydrophilic–lipophilic balance (HLB) of APG1214. It was found that the hydrophob-hydrophob interactions between the hydrophobic moieties of the HMPA backbone and the alkyl chain of APG1214 result in a mixed micelle formation, serving as junction points for supramolecular network formation accompanied by a pronounced increase of the apparent solution viscosity. Earlier [45, 46] the synthetic strategy of a series of polymeric betaines based on aminocrotonates and unsaturated carboxylic acids were developed. Among them, a special attention was paid to hydrophobic polybetaines containing long alkyl chains C₁₂H₂₅, C₁₃H₂₇, C₁₄H₂₉, C₁₆H₃₃, and C₁₈H₃₇ and named as CRODDA-MAA, CROTriDA-MAA, CROTDA-MAA, CROHDA-MAA and CROODA-MAA, respectively, in dependence of the length of alkyl chains (**Figure 9**).



Figure 9. Formation of hydrophobically modified polymeric betaines from alkylaminocrotonates and methacrylic acid via Michael addition reaction.

In aqueous KOH the hydrophobic groups tend to form intra-macromolecular micelle or intermacromolecular vesicle stabilized by hydrophobic interactions of long alkyl groups (Figure 10) [47].



Figure 10. Schematic representation of formation of micellar and vesicular structures of hydrophobic polybetaines and TEM pictures of CROHDA-MAA (a) and CROTDA-MAA (b) in aqueous KOH solutions at C=15 mg·mL⁻¹.

The existence of such structures is visualized by cryo-TEM measurements. The colloidal particles have uniformed spherical or toroidal-shaped forms. The size of uniformed micelles is about 140-150 nm, while the outer diameter of toroidal-shaped micelle is 165 nm with its internal diameter 50 nm. The efficiency of the hydrophobic polymeric betaine bearing $C_{16}H_{33}$ group (CROHDA-MAA) was tested as a prototype alkaline-surfactant-polymer (ASP) flooding agent with respect to the heavy oil of Karazhanbas oilfield (Western Kazakhstan) [39, 48]. Results of sand pack flooding experiments showed that in the case of injection of a 0.5% solution of CROHDA-MAA dissolved in a 0.5 % aqueous KOH solution yielded up to a 37% oil displacement coefficient. In aqueous KOH, the CROHDA-MAA is able to form micellar or vesicular structures stabilized by intramolecular or intermolecular hydrophobic interactions of long alkyl chains. Since the CROHDA-MAA in aqueous KOH can exist in the forms of micron- and nanosized micelles and vesicles consisting of hydrophobic a core and a hydrophilic edge, the oil droplets adsorbed on the rock can imbibe into the hydrophobic pockets forming o/w microemulsions. In the vicinity of rock/oil boundary, the long alkyl chains are probably inverted and dipped into oil environment, decreasing the interfacial tension, entrapping and sweeping the oil droplets, then entrain along with the flowing aqueous phase (Figure 11).



Figure 11. Schematic representation of oil recovery by polybetaine "soap" – CROHDA-MAA.

Partial unfolding of "polysoap" macromolecules near rock/oil boundary may occur due to preferentially oil-wetness of hydrophobic groups and solvation of betaine parts by water. Thus, the hydrophobically modified polymeric betaines consisting of hydrophobic "tail" and hydrophilic "head" can play the role of "polysoap" acting as polymer, surfactant, and alkaline simultaneously and may be perspective materials for heavy oil displacement due to the combination of the advantages of ASP flooding and exhibiting the synergistic effect [49]. According to the results of Gou *et al.* [50] the additional amount of oil recovered by hydrophobically modified polyampholyte based on acrylamide, sodium acrylate, 3-(diallylamino)-2-hydroxypropyl sulfonate, and 3-(2-(2-heptadec-8-enyl-4,5-dihydro-imidazol-1-yl)ethyl-carbomoyl)acrylic acid was equal to 15.46%. HMPA with zwitterionic betaine groups reported by authors [51] showed salt thickening behavior; a salt thickening mechanism was proposed that the destroyed inner salt bond of zwitterionic betaine groups in salt solution (which is named as anti-polyelectrolyte or "salting-in" effect) brought a greater hydrodynamic diameter of polymer molecules, and the inter-molecular hydrophobic interaction of the long alkyl groups in salt solution produced a stronger hydrophobic

association. Analogous salt-thickening behavior exhibited the copolymer of acrylamide and Nmethyl-N-allyllauroylpropanesulfonate containing 3 mol.% of both betaine and hydrophobic groups [52]. The core flooding tests and microscopic displacement experiments showed that HMPA had salt thickening property and anti-scouring capacity in porous medium in high salt reservoirs and was able to recover 23.7% oil after the water flooding stage. Zwitterionic sulfobetaine-unit incorporated HPAM increases the viscosity under high salinity and high temperature and shows a good viscosity retention at 90°C in a synthetic brine of 200 g·L⁻¹ salinity that is significant for the EOR [53]. A heat-, salt- and pressure resistant amphoteric hydrogel composed of acrylamide (AAm), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and Nacryloyl morpholine (ACMO) and gelled at 150 °C was able to plug fractures of 0.1-5.0 mm leading to the breakthrough pressure exceeded 4.0 MPa [54]. After aging at 150 °C for 7 days, the elastic modulus of AAm-AMPS-ACMO only decreased by 14.29%. The gel strength and gelation time of amphoteric gel could be adjusted by terpolymer concentration, cross-linker concentration, temperature, and salinity, which was beneficial to enter and plug fractures smoothly. Extensive laboratory experiments indicated that amphoteric gel has outstanding thermal stability and pressure-bearing performance, making it a promising candidate for lost circulation control in hightemperature and high-pressure formations. A series of AAm-co-AAc-co-DMAEM terpolymer hydrogels complexed with Cu²⁺ considerably enhanced the strength of network due to complexation between Cu^{2+} and the carboxyl groups of acrylic acid (AAc) [55]. Further the polyampholyte-Cu²⁺ hydrogel powder was used for plugging the microcracks inside the cement annulus and solidified to form cement stone. Once microcracks occur inside the cement paste, the natural gas with associated CO₂ comes into contact with the polyampholyte-Cu²⁺ hydrogels. As a result, the polyampholyte-metal network is triggered by CO_2 due to protonation of the tertiary amine groups of the DMAEMA by acidic carbon dioxide gas. The polyampholyte hydrogels swell because of anti-polyelectrolyte effect and effectively plug the microcracks inside the cement paste. For conformance control in oil recovery authors [56] suggested to apply the crosslinked amphoteric terpolymers of AAm-AMPS-APTAC containing bentonite. The mechanical strength of composite hydrogels increased from 82.3 Pa to 173.7 Pa in the presence of 5 wt.% bentonite. The swelling degree (SD) of AAm-AMPS-APTAC-Bentonite hydrogels increases in saline water (total salinity of reservoir water is 61 and 128 g·L⁻¹), two times increases upon heating up to 80 °C, less sensitive to pH change at the interval of pH 4.5-9.0, and collapses when the content of organic solvents (ethanol and acetone) is more than 50 or 60 vol.% in water-organic solvent mixture. Collapsing polyampholyte gels in organic solvents are important for removing blockages in the oil reservoir in the case of an emergency. All these properties are suitable for application of amphoteric hydrogels in conformance control and oil recovery. The ampholytic carboxymethyl chitosan biopolymer containing graphene-oxide (GO) and functionalized carbon nanotubes (CNT) was used as preformed particle gels (PPGs) for the possible application in water shut-off applications [57] (Figure 12).



Figure 12. Chemical structure of carboxymethyl chitosan along with their positive and negative ionizable groups.

The thermal and salt responsive amphoteric nano- and microgels are insufficiently studied objects, especially in the context of enhanced oil recovery depending on temperature and salt additive. Amphoteric nano- and microgels based on AAm₈₀-APTAC₁₀-AMPS₁₀ exhibited the best swelling capacity and viscosifying effect in saline water [58-61]. From TEM images it can be observed that these samples have spherical shape and contain both nanogels and microgels (Figure 13).



Figure 13. TEM images of nano- and microgels of AAm₈₀-APTAC₁₀-AMPS₁₀.

The swelling capacity of AAm_{80} -APTAC₁₀-AMPS₁₀ microgels upon salt addition was evaluated [61]. In the range of 0.1-4.0 M NaCl the average hydrodynamic size of microgel particles R_h and dynamic viscosity linearly increases due to "antipolyelectrolyte effect". In 4.0 M NaCl the R_h of microgel particles and the dynamic viscosity increases 2.5-2.7 times compared to 0.1 M NaCl. The ability of polyampholyte microgels to swell and be effective viscosity enhancers in high-salinity and high-temperature reservoirs may play a crucial role in oil recovery. In our experiments the 2,500 ppm AAm_{80} -APTAC₁₀-AMPS₁₀ microgel suspension in 136 g·L⁻¹ brine was injected into the sandstone core sample equipped with two pressure measurement taps for experiments. (Figure 14).



Figure 14. Core holder (model) equipped with 2 pressure sensors (a); core face (b); layout of core holder connected to a personal computer (c) and microgel particles dissolved in 136 g·L⁻¹ brine (d).

Figures 15, 16 show pressure readings taken during the injection of brine and microgel suspension into the core.



Figure 15. Pressure readings at the inlet and center of the core during oil displacement with brine (water flooding)

Figure 16. Pressure readings at the inlet and center of the core during injection of 2,500 ppm microgel

Table 1 shows stabilized pressure readings which were used to calculate the resistance and residual resistance factors.

Table 1. Stabilized pressure readings observed during water flooding, microgel injection and post-flush

Water flooding		Microgel injection		Post-flush	
P inlet, MPa	P center,	P inlet, MPa	P center,	P inlet, MPa	P center, MPa
	MPa		MPa		
0.324	0.067	0.545	0.097	0.621	0.095

Figure 17 shows the results of resistance and residual resistance factors calculated for different parts of the core.



Figure 17. The values of resistance (RF) and residual resistance (RRF) factors calculated for different parts of core samples

It should be noted that for the 1st half of the core RRF was higher than RF. This may be explained by the swelling of the microgels during 24 h aging period. For the second part of the core RF and RRF were almost equal. This result can be explained by stabilization of microgel particles in brine solution and reduction of the permeability. Amphoteric nanospheres with a small particle size (~ 50 nm) and spherical shape were prepared by using an acrylamide (AAm), 2-acrylamide-2-methylpropanesulfonic acid (AMPS), diallyl dimethylammonium chloride (DMDAAC), and methylene-bis-acrylamide mixed solution as the aqueous phase and Span-80 and Tween-80 as the composite emulsifier, followed by reverse-phase microemulsion polymerization [62]. The plugging test showed that the amphoteric nanospheres achieve a certain degree of plugging of cores, with an average plugging rate of 79.5%. The oil displacement test results show that under certain conditions, the effect of nanospheres on oil displacement is improved with decrease in core permeability. The average recovery rate of each low permeability core after injection of AAm-AMPS-DMDAAC nanospheres was equal to 13.46%.

Interpolyelectrolyte complexes (IPEC) – the products of electrostatic interaction between oppositely charged polyelectrolytes – may open a new pathway for polymer flooding as thickeners in high-salinity conditions. A polyelectrolyte complex was prepared from anionic poly(acrylamide-*co*-acrylic acid-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) (PA3) and cationic poly((2-methacryloyloxyethyl) trimethyl ammonium chloride) (PDMC) [63] (Figure 18).



Figure 18. Structural units of anionic poly(acrylamide-*co*-acrylic acid-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) (PA3) and cationic poly((2-methacryloyloxyethyl) trimethyl ammonium chloride) (PDMC) used for fabrication of IPEC

The viscosity of the PA3/PDMC complex initially decreases upon the addition of NaCl, it then increases at a higher NaCl dosage. More significantly, this salt-induced viscosification leads to a high viscosity in a saturated oilfield brine, with a remarkable heat- and shear-resistance and proppant carrying capacity in comparison to the common HPAM-based system. The PA3/PDMC complex exhibited unique salt-induced viscosifying behavior at high salt concentrations dictated by two synergistic effects: the recovery of charge – charge repulsion and the electrostatic attractive forces created by the oppositely charged counter ions.

Conclusion

The fundamental and application aspects of annealed and quenched polyampholytes, polymeric betaines, hydrophobic polyampholytes as well as nano- and microgels, preformed particle gels, interpolyelectrolyte complexes are briefly outlined in this communication. The main attention is paid to so called "antipolyelectrolyte effect" that enhances the viscosifying of high saline and high temperature oil reservoir for utilization in EOR processes.

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