Polymer Degradation and Stability 121 (2015) 69–77

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Theoretical studies of hydrolysis and stability of polyacrylamide polymers

Qisheng Ma [a, b], Patrick J. Shuler [a], Carl W. Aften [a], Yongchun Tang [b, *]

[a] *ChemEOR Inc., Covina, CA 91722, USA*
[b] *Power Environmental Energy Research Institute, Covina, CA 91722, USA*

ARTICLE INFO

Article history:
Received 3 June 2015
Received in revised form
17 August 2015
Accepted 18 August 2015
Available online 24 August 2015

Keywords:
Polyacrylamide
Hydrolysis
Stability
Density functional theory (DFT)
Cation ions

ABSTRACT

Thermal stability of water-soluble polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) polymers under various solution conditions have been studied utilizing Quantum Mechanics Density Functional Theory (DFT) computational modeling method. The hydrolysis reaction of the amide group (AM) to form acrylic acid (AA) is significantly affected by the pH of solution and the presence of cationic species such as Ca^{2+}. Without catalyzed, PAM is thermally stable with transition barriers as high as 50 kcal/mol. Both acid and base can catalyze the hydrolysis reaction by lowering activation energies with more than 10 kcal/mol. Formation of the 6-membered ring transition state (TS) structure arising from the assist of a second water or an ammonia molecule yields a lower enthalpic energy, which is sufficient to overcome the entropic penalty for bring three molecular species together for reactions. Ammonia/ammonium as products of hydrolysis also catalyze the reaction, rendering an auto-accelerated amide hydrolysis kinetics. The divalent Ca^{+2} cation not only interacts with carboxylic groups on HPAM to alter their rheological and phase behaviors, but also catalyzes the hydrolysis reaction to increase the degree of hydrolysis of HPAM. These results provide theoretical insights for molecular modifications of PAM/HAPM for their high-temperature (HT) and high-salinity (HS) applications.

1. Introduction

Water-soluble polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) polymers are among the most commonly used chemicals in oilfield applications. In polymer-augmented water-flooding Enhanced Oil Recovery (EOR) processes, HPAM polymers are often used as mobility-control agents to increase the viscosity of stimulation fluids in order to improve the sweep efficiency [1–3]. In hydraulic fracturing reservoir treatments, high molecular-weight PAM/HPAM are used as friction reducers in order to minimize pumping power demands and to provide sufficient proppant-carrying capacity of fracturing fluids [4–6]. However, applications of PAM/HPAM in high-temperature (HT) (>90 °C) and high-salinity (HS) (100,000–200,000 ppm) reservoir conditions are limited primarily because of their thermal instability [7–9]. This is particularly the case when there are certain amounts of divalent cations (Ca^{2+}, Mg^{2+}, Sr^{2+} and etc.) in reservoir brines [10–12]. It is well documented that cationic species strongly interact with HPAM, resulting in the rapid phase separation through formation of gel or precipitate [7,13,14]. Multivalent cations are easily chelated by HPAM chains to form a stable cross-linking complexes such as CaO_4 [15]. A recent laboratory study conducted by Seright et al. [16] indicated that a PAM polymer can remain thermally stable in the absence of dissolved oxygen and divalent cations, so that the HPAM solution is projected to maintain at least half of their original viscosity for over 8 years at 100 °C and about 2 years at 120 °C. Moradi-Araghi and Doe [12] shown that stability limitations of PAM significantly varied in brines containing different divalent cations (<96 °C for 270 mg/L; <88 °C for 500 mg/L; and <75 °C for 2000 mg/L). These observation indicate significant adverse effects of divalent cations on the stability of PAM/HPAM polymers.

The dangling amide group of the PAM polymer could be hydrolyzed to form an acrylic acid that is subject to the easier interaction with cations. Chemistry regarding the amide hydrolysis is very rich and has been considered as an important modeled reaction for the enzymatic cleavage of peptide bonds [17–19]. Mechanism and kinetics of the amide hydrolysis under different conditions have been extensively studied from both experimental

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* Corresponding author. Power Environmental Energy Research Institute, 738 Arrow Grand Circle, Covina, CA 91722, USA.
E-mail address: tang@peeri.org (Y. Tang).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.08.012

and theoretical aspects. For example, theoretical studies of the base-catalyzed amide hydrolysis reaction predicted a 20–30 kcal/mol transition barrier that is in good agreement with experimental measurements [20,21]. A two-step mechanism involving the nucleophilic attack of hydroxide ion on the carbonyl carbon to form a tetrahedral intermediate as the first step, followed by the release of an ammonia molecule, has been established [22–26]. Acid-promoted amide hydrolysis reactions have also been studied [18,27–30]. O- and N-protonation pathways were found to compete with either other, with similar activation energies of ~20 kcal/mol, which are consistent with the experimental value of 21.5 kcal/mol [31,32].

Under the neutral condition, interaction of the amide group with a water molecule is much more difficult, without assisted or catalyzed. Both concerted and stepwise pathways yield quite high activation energies (>50 kcal/mol) in gas-phase and in aqueous phase [28,33–35]. The reverse hydrolysis reaction has also been studied, and activation energies are also very high [36–38]. On the other hand, Oie et al. [37] found that the assistance of an additional ammonia molecule could substantially lower activation barriers for both of stepwise (−10 kcal/mol) and concerted (−2 kcal/mol) pathways. Mechanisms of the water-promoted amide hydrolysis by a second water molecule have also been proposed [29,33,39–42]. The presence of additional water molecule might reduce activation energies in range of 15–20 kcal/mol. Such a water assistance effect is found to be more profound in the acid-promoted reaction [33], i.e., the O-protonation facilitates the water-assisting hydrolysis reaction, such that to significantly lower the activation energy by as much as 35 kcal/mol.

Despite intensively studies on the amide hydrolysis, there is relatively less attention paid to understand cationic effects on the reaction mechanism. In particular, there still is a lack of fundamental understanding on why the presence of different concentrations of Ca^{+2} could have such adverse effects on the thermal stability of PAM, which is considered as the main factor limiting applications of PAM/HPAM under high-temperature/high-salinity (HT/HS) environment. Therefore, our objective is to conduct a systematic study of the amide hydrolysis under different conditions, with an emphasis on effects of divalent cations. Molecular simulations based on Density Functional Theory (DFT) methods are applied to map out possible reaction pathways and to determine the configuration energies of all stable, intermediate and transition states. Our results indicate that, in addition to aggravate precipitation, divalent cations in aqueous solution might also catalyze the amide hydrolysis reaction. These results offer a plausible explanation to the laboratory and field observations that the thermal stability of PAM polymers is significantly lowered when there are higher concentrated divalent cations in brines.

2. Computational methods

PAM is composed of repeating units of the acrylamide (AM) (Fig. 1(a)). At elevated temperature, some of amide groups undergo the hydrolysis reaction to become carboxylic groups (Fig. 1(b)). The degree of hydrolysis τ of HPAM (Fig. 1(c)) is defined as:

$$\tau = \frac{Y}{X+Y}; \quad 0 \le \tau \le 1 \tag{1}$$

Where X and Y are numbers of amide and carboxylic groups in polymer. Because our studies mainly focus on the hydrolysis reaction of the amide group, we model the PAM with a dangling $-CONH_2$ group attaching to the middle carbon of the C_5 molecule. Therefore we have neglected the possible neighbor group interactions in this study.

Molecular geometry of all reactants, intermediates, transition states and products are fully optimized using the quantum mechanics DFT/B3LYP/6-31G** method. Since there are mainly organic elements (C, O, N, and H) involved, such a level of computation has been well established producing reasonable results for both energetic and geometric information of chemical reactions. Thermodynamic calculations were carried out to take the Zero-Point Energy (ZPE) correction and the temperature dependence into accounts. All configurations have been identified as local minima (no imaginary vibrational modes for stationary states and unique imaginary vibrational frequency for a transition state). The water solvation effect is also considered using the continuum-solvation approach by solving the Poisson–Bolzmann equation with a default dielectric constant of 80.37 and a probe radius of 1.40 Å for water. From previous studies, we found no significant deviation in structures between the gas-phase and continuum-solvation phase, so a single point solvation energy correction is considerably sufficient. Therefore, the molecular geometry is only optimized in gas-phase, while the solvation energy determined from the gas-phase geometry is included as an additional energy term E_{sol}. The Gibbs' free energy is determined from:

$$\Delta G_T = E_0 + ZPE + \delta H_T - T\delta S_T + E_{sol} \tag{2}$$

where E_0 is the total gas-phase electronic energy at temperature T = 0 K, ZPE is the quantum mechanics Zero-Point Energy (ZPE) correction, δH_T and δS_T are the enthalpy and entropy changes from temperature = 0 to T, and E_{sol} is the single solvation energy correction. All calculated energies are taken at the ambient condition (T = 298.15 K, P = 1 atm). And the commercial Quantum Mechanical computational software, Jaguar was used.

3. Results and discussions

3.1. Hydrolysis of PAM under the neutral condition

Under neutral conditions, two competitive reaction paths are considered (Fig. 2). The two-step pathway (a) features a nucleophilic addition of one water molecule to form a T-complex through

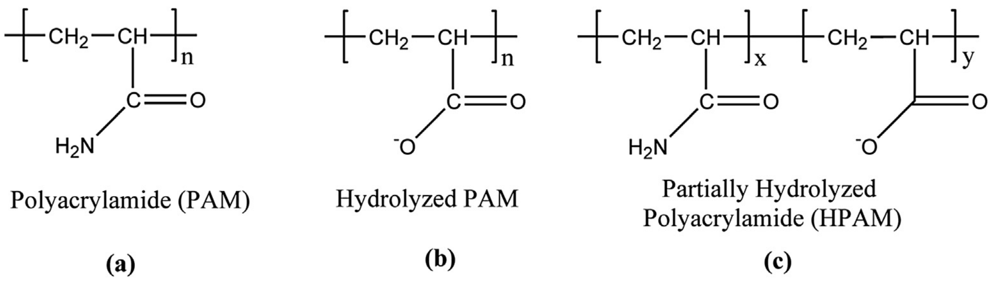

Fig. 1. Molecular structures of (a) Polyacrylamide (PAM), (b) Hydrolyzed Polyacrylamide, and (c) Partially Hydrolyzed Polyacrylamide (HPAM).