Theoretical Studies of Hydrolysis and Stability of Polyacrylamide Polymers

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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/HPAM 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) ($> 90^{\circ}\text{C}$) 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 ($< 96^{\circ}\text{C}$ for 270 mg/L; $< 88^{\circ}\text{C}$ for 500 mg/L; and $< 75^{\circ}\text{C}$ for 2,000 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 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) (**Figure 1(a)**). At elevated temperature, some of amide groups undergo the hydrolysis reaction to become carboxylic groups (**Figure 1(b)**). The degree of hydrolysis τ of HPAM (**Figure 1(c)**) is defined as:

$$\tau = \frac{Y}{X + Y}; \quad 0 \leq \tau \leq 1 \quad (1)$$

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 $-\text{CONH}_2$ group attaching to the middle carbon of the C_5 molecule. Therefore we have neglected the possible neighbor group interactions in this study.

Figure 1: Molecular Structures of (a) Polyacrylamide (PAM), (b) Hydrolyzed Polyacrylamide, and (c) Partially Hydrolyzed Polyacrylamide (HPAM)

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-Boltzmann 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:

$$\Delta G_T = E_0 + ZPE + \delta H_T - T\delta S_T + E_{sol} \quad (1)$$

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 (**Figure 2**). The two-step pathway (a) features a nucleophilic addition of one water molecule to form a T-complex through transition state TS_1 , followed by the ammonia elimination *via* transition state TS_2 . The concerted pathway (b) is characterized by simultaneous C-O and N-H bond formations, and the C-N bond breaking through transition state TS_3 . For both pathways, the net reaction is the same:

Calculated transition barriers of both reaction pathways are very high (> 50 kcal/mol), indicating that the hydrolysis of PAM under the neutral condition is difficult.

3.2 The General Base-Catalyzed Mechanism

The general base-catalyzed mechanism is well-documented, whereas a strong basic aqueous solution (the hydroxide OH^-) is required.

The two-step stepwise pathways with the first step of the nucleophilic addition of an OH^- group onto the carbonyl carbon with a transition barrier of 22.3 kcal/mol (TS_4), followed by the ammonia elimination with a transition barrier of 31.5 kcal/mol (TS_5)

(**Figure 3**). Our calculated results are in general agreement with the experimental data by Guthrie [20] in where they found transition energies are in range of 20 ~ 30 kcal/mol at 25 ~ 100 °C for the base-catalyzed amide hydrolysis.

3.3 Acid-Catalyzed Mechanism – N-Protonation vs. O-Protonation

Under the acidic condition, hydrolysis could be initiated from either the N-protonation (proton attacking the NH₂ group) or O-protonation (proton attacking the carbonyl oxygen) (**Figure 4**). Our results indicate that both O- and N-protonation pathways have similar transition barriers of > 40 kcal/mol. The initial O-protonation is more energetically favorable with a formation energy of -8.7 kcal/mol compared to the -0.8 kcal/mol for that of N-protonation. However, the transition barrier of the nucleophilic addition along the O-protonation pathway is 37.5 + 8.7 = 45.2 kcal/mol which is slightly higher than the N-protonation pathway 41.0 + 0.8 = 41.8 kcal/mol.

3.4 Water-Assisted Concerted Mechanism under the Neutral Condition

The concerted pathway under the neutral condition (*ref.* **Figure 2** (b)) involves a 4-membered ring structure in the transition state, which is typically more energy-intensive. One possible path having a lower transition barrier is with the assist of an additional water molecule to form a 6-membered ring transition state (**Figure 5**). Normally it requires a large entropy penalty to bring together of three molecular species for reaction. On the other hand, the formation of a 6-member ring structure facilitates the prton transfer and rearrangement to lower the enthalpy barrier. The final Gibbs' energy gain/loss will be determined from the competition of enthalpy and entropy changes. In this case, the formation of the 6-membered ring transition state lowers the overall transition barrier (42.4 kcal/mol), compared to 57.8 kcal/mol for the non-assisted neutral pathways. The overall reaction of the water-assisted hydrolysis is expressed as follow:

Herein, the second water molecule (in bold) acts as an aid (catalyst) to lower the transition barrier, without being consumed or transformed.

3.5 Auto-Accelerated Hydrolysis Mechanism – Ammonia-Assisted Pathways

Analogous to the neutral water-assist pathway, the ammonia-assisted mechanism has also been considered (**Figure 6**). Both the concerted and stepwise pathways have the same overall reaction:

Here again, the ammonia molecule aids the reaction similar to the water molecule in the water-assisted mechanism. For the concerted pathway, the energy-lowering effect of the ammonia-assisted pathway (46.8 kcal/mol) is relatively weaker than the water-assisted pathway (42.4 kcal/mol, *ref.* **Figure 5**). The stepwise pathway has the lower transition barrier (37.8 kcal/mol) than the concerted pathway (46.8 kcal/mol). A special feature of the ammonia-assisted pathway is that the ammonia itself is the end product of reaction. This suggests that the amide hydrolysis will be an auto-accelerated reaction, i.e., the formation of the ammonia as a product could also act as a catalyst to increase the reaction rate of hydrolysis.

3.6 Protonated Water-Assisted Mechanism

The water-assisted mechanism can have more profound impacts on the amide hydrolysis under the acidic condition. A protonated water-assisted reaction is initiated by O-protonation, followed by the 6-membered ring transition state (**Figure 7**). The overall reaction is:

The transition barrier is significantly lowered, with the 18.75 kcal/mol (TS₁₄) higher than the initial reactant configuration. Even if we take into account of -8.7 kcal/mol energy-gain from O-protonation, the overall transition barrier of 27.5 kcal/mol is still very energetically favorable.

3.7 Ammonium Catalyzed Water-Assisted Mechanism

The positively charged ammonium cation (NH₄⁺) can also attack on the carbonyl oxygen to facilitate the water-assisted hydrolysis pathway (**Figure 8**). The overall reaction is:

The overall transition barrier of 27.2 kcal/mol is comparable with that with the protonated water-assisted pathway (27.5 kcal/mol). Note that the ammonia (NH₃) has a pK value of 9.25. Even under the neutral condition, nearly 99% of ammonia exists in the protonated state, e.g., NH₄⁺. Therefore, this auto-accelerated effect from the ammonia production will be more significantly. Instead of acting as a neutral ammonia to accelerate the amide hydrolysis with the lowest transition barrier (37.8 kcal/mol, *ref.* **Figure 6**), the

ammonium cation can further lower the transition barrier to 27.2 kcal/mol through the protonated water-assisted pathway, even under the neutral condition.

3.8 Cation-Catalyzed Water-Assisted Mechanism

In both protonated water-assisted and ammonium-catalyzed water-assisted pathways, the initial attacking of positively charged species on the carbonyl oxygen plays a significant role. Upon protonated, the carbonyl carbon becomes more positively charged, which substantially weakens the C-N bond to facilitate the release of the -NH_3 group. This result suggests that the presence of divalent cations such as Ca^{+2} or Mg^{+2} that can also attack to the carbonyl oxygen to catalyze the amide hydrolysis reaction (**Figure 9**). Indeed, the calculated transition barrier for the Ca^{2+} -catalyzed water-assisted hydrolysis reaction has a very low value of $11.5 + 6.3 = 17.8$ kcal/mol. This result indicates that cations such as Ca^{2+} can not only act as a sink to precipitate HPAM, it can also catalyze the hydrolysis reaction to aggravate the formation of carbonyl group on HPAM.

4. Conclusion

Thermal stability of PAM/HPAM under HT/HS environments is one of the most important factors preventing widespread oilfield applications of PAM chemicals in harsh reservoir conditions. Structural modifications of PAM to form substituted and/or associated polymers have shown potentials to improve their thermal stability [43-46]. For example, substitutions of the H-atom at the NH_2 group with more shear-resistant functional groups such as longer alkyl chains and N-substitutes offer higher thermal stability in solution [47]. Water-soluble hydrophobically associating polymers contain a small number of hydrophobic groups directly attached to the polymer backbone. In aqueous solutions, these add-on hydrophobic groups have potential to associate resulting in an increasing solution viscosity [48-51]. Fundamental understanding of the basic chemistry related to the amide hydrolysis mechanism is of great importance to the molecular design and syntheses of modified PAM and their oilfield applications, particularly under HT/HS reservoir conditions.

In **Table 1**, we list all calculated transition barriers of the amide hydrolysis under different conditions from this study. Highlights of results are as follows:

- Both base- and acid-catalyzed reactions have transition barriers in range of 20~30 kcal/mol, which are much lower than the un-catalyzed reactions (40~50 kcal/mol)

under the neutral condition. These results are consistent with the experimental observations that thermal stability of PAM polymers is very sensitive to salinity and pH of the aqueous solution.

- Both water and ammonia molecules can assist the amide hydrolysis. Because ammonia is one of end products of the hydrolysis reaction, the reaction is considered as auto-accelerated that the continuous accumulation of ammonia (or in its ionic ammonium form) will aggravate the degree of hydrolysis of PAM.
- The initial interaction of the positive species with the carbonyl oxygen is an important step to further lower the transition barrier of the water-assisted hydrolysis. The weaker C-N bond resulting from more positively charged carbonyl carbon is considered as one of the reasons for the lowering barriers. Interactions of positively charged species with the carbonyl oxygen could occur from the O-protonation initiated from H_3O^+ under the acidic condition, or from NH_4^+ produced from hydrolysis, or in the presence of different concentrations of divalent cations such as Ca^{+2} , Mg^{+2} .
- In principal, the PAM hydrolysis could be slowed down if we can protect the carbonyl oxygen from attacking of the positive species. For instance, molecular modification of PAM/HPAM could be done by introducing the steric hindrance effects to prevent carbonyl oxygen from exposure, or by designing bridging groups to link the carbonyl oxygen with neighboring groups.
- Water-assisted pathway also plays an important role in the amide hydrolysis reaction. Therefore, by introducing the hydrophobic functional groups, such as Diacetone Acrylamide (DAAM), 2-Acrylamido-2-methylpropane sulfonic acid (AMPS), or N-Vinylpyrrolidone (NVP), onto PAM/HPAM polymers, we would expect to increase the entropy penalty for bringing the second water molecule into reaction, such that to slow down the amide hydrolysis reaction.
- The divalent cations such as Ca^{2+} and Mg^{2+} presented in brines have significantly adverse impacts on the thermal stability of PAM/HPAM. These cations not only can form complexes (gels or precipitates) with the carboxylic groups with HPAM to alter their rheological and phase properties, they can also catalyze the amide hydrolysis reaction to increase the degree of hydrolysis of PAM/HPAM polymers. In order to

apply PAM/HPAM polymers in high-temperature/high-salinity (HT/HS) reservoir conditions, it is important to mitigate cationic effects on hydrolysis and stability. This can also be achieved by the addition of certain amounts of cation scavengers such as sodium sulfate (Na_2SO_4), low-molecular weight PAM/HPAM or acetic acid to react with divalent cations.

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Table 1: Summary of the Calculated Activation Energies of the Amide Hydrolysis of PAM under Different Conditions. All energies are taken at the room temperature $T = 298.15$ K and ambient pressure (1 atm).

Reaction Condition	Reaction Pathways	Activation Energy (kcal/mol)
Neutral	Stepwise	54.4
	Concerted	57.8
	Water Assisted	42.4
	Concerted Ammonium Assisted	46.8
	Stepwise Ammonium Assisted	37.8
	Water-assisted Ammonium Catalyzed	27.2
	Water-assisted Ca^{+2} -catalyzed	17.8
Basic	General Stepwise	31.5
Acidic	O-protonation	46.2
	N-protonation	41.8
	Water Assisted	27.5

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Figures and Captions

Figure 1

Polyacrylamide (PAM)

(a)

Hydrolyzed PAM

(b)

Partially Hydrolyzed
Polyacrylamide (HPAM)

(c)

Figure 1: Molecular Structures of (a) Polyacrylamide (PAM), (b) Hydrolyzed Polyacrylamide, and (c) Partially Hydrolyzed Polyacrylamide (HPAM)

Figure 2

Figure 2: Reaction pathways of the amide hydrolysis under the neutral condition for both the (a) stepwise and (b) concerted mechanisms. The numbers inside the parenthesis are the relative energies related that of the separated molecules.

Figure 3

Figure 3: Reaction pathway of the amide hydrolysis reaction under base-catalyzed condition by the stepwise mechanism.

Figure 4(a)

Figure 4(a)

Figure 4(b)

Figure 4: Reaction pathways of the amide hydrolysis reaction under acidic conditions initiated from (a) O-Protonation and (b) N-Protonation.

Figure 5

Figure 5: Reaction pathway of the water-assisted hydrolysis reaction under the neutral condition.

Figure 6

Figure 6: Reaction pathways of the ammonia-assisted hydrolysis reaction under the neutral condition (a) the stepwise pathway and (b) the concerted pathway.

Figure 7

Figure 7: Reaction pathway and the calculated energy profile of the water-assisted O-protonation hydrolysis reaction.

Figure 8

Figure 8: Reaction pathway of the water-assisted hydrolysis pathway initiated from the interaction of ammonium ion (NH_4^+) on the O-atom.

Figure 9

Figure 9: Reaction pathway and the calculated energy profile of water-assisted hydrolysis pathway initiated from the Ca^{2+} cation attacking on the O-atom.