

Effect of Ionic Strength on the Reactivity Ratios of Acrylamide/Acrylic Acid (sodium acrylate) Copolymerization

Marzieh Riahinezhad, Niousha Kazemi, Neil McManus, Alexander Penlidis

Department of Chemical Engineering, Institute for Polymer Research (IPR), University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Correspondence to: A. Penlidis (E-mail: penlidis@uwaterloo.ca)

ABSTRACT: The ionic strength (IS) of polyelectrolyte solutions plays an important role in influencing reaction kinetics. The largely unstudied effect of IS on monomer reactivity ratios and copolymerization rates of acrylamide (AAM) and acrylic acid (AAc), in the form of sodium acrylate (NaAc), is investigated. Salt addition affects the nature of overall charges of the polyelectrolyte solution and diminishes the electrostatic repulsions between reacting chains. Therefore, changing the IS of the solution by incorporating salts affect not only the point estimates of the monomer reactivity ratios but also the overall behavior of the copolymerization (with a transition to azeotropic behavior). Experimental results on copolymerization rates confirm the observed trends in reactivity ratio behavior. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40949.

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INTRODUCTION

Radical copolymerization of acrylamide (AAM) and acrylic acid (AAc), in the form of sodium acrylate (NaAc), in water is quite challenging because of the polyelectrolyte nature of the system. For aqueous copolymerization of AAM/AAc (acrylic acid in the form of sodium acrylate, NaAc), the nature of the reaction medium plays an important role, in terms of such factors as degree of ionization of monomers, polarity of the solvent, pH, and ionic strength (IS) of the solution. This is because the balance of all these factors dictates the proportions of the various ion forms of the reactants (monomers and macroradicals), with a subsequent bearing on the overall reaction.¹ This is probably one of the main reasons that the monomer reactivity ratios for this copolymerization are highly inconsistent in the literature.² The monomer reactivity ratios (r_1 and r_2), well-known indicators of monomer reactivity characteristics, are defined as ratios of the homopropagation rate constant over the cross-propagation rate constant for each monomer.

Acrylic acid monomer, AAc, is a weak acid which dissociates slightly in water.^{3–5} The value of pKa, ($-\log(K_a)$), for AAc monomer is 4.2. Poly(acrylic acid), PAAc, is also a poor proton donor (weak acid) with a pKa value of 4.75. In polyelectrolyte solutions, there is a correlation between pH and pKa of the acid based on the well-known Henderson-Hasselbach equation. Hence, the pH of a solution and the dissociation constant (K_a), dictate the degree of ionization of the acid. Considering the

pKa values for AAc monomer and polymer, it is obvious that the degree of ionization is greater for monomeric AAc compared to PAAc (at constant pH). Throughout the calculations of the paper, the ionization of AAc monomer in the beginning of the reaction is considered.

At low pH (around 2), AAc is nonionized. As pH increases, by adding base to the system, the degree of dissociation increases, until AAc is fully ionized to acrylate at pH values greater than 6.⁶ When additional counterions are present in the solution, there are effects from ion pairing and shielding of the anionic charge of acrylate by those other counterions. In aqueous salt solutions, the acrylate ion is surrounded by two layers, based on what Ikegami showed for hydration and ion binding of AAc in the presence of sodium chloride salts.⁷ In the first layer, which is called “intrinsic hydration region,” the acrylate ion is surrounded by water molecules. This layer is surrounded further by a second layer, where cations are localized by a condensation phenomenon (this is a feature of highly charged polyelectrolytes). So, one can visualize this as if the acrylate anion (either monomer or radical) is surrounded by other molecules and ions within two cylinders, where hydration with water molecules and ion binding with cations happen, respectively.

During polymerization, the negative charges on the acrylate monomers and growing radicals cause electrostatic repulsions between them. These repulsions make reactive interactions less favorable. In relation to this, it has been claimed that the

shielding of like charged anions by cations (e.g., salts) dissipates the degree of electrostatic repulsion between charged groups.^{8,9} As a result of this shielding, IS becomes an important factor for polymerizations involving ionic monomers.

IS can be evaluated based on the ions present in the solution. In the case of AAm/NaAc copolymerization, the ions present are ionized AAc (or acrylate anion) and the selected cation. Since IS depends on the concentration of acrylate monomer in the system, it can change during polymerization. All reported IS values in this study were considered in the beginning of the polymerization.

It should be mentioned that not only does the ion charge number play a role in ion shielding, but also the type of the cation, which affects the electrostatic attraction between anion and counterions. It has been shown that the reactivities of both AAm and AAc in the system are affected by the type of cation.^{8,10} The effect of the nature of the dissolved ionic species on rate naturally extends into copolymerizations.

Having made these introductory statements, it is important to understand how IS acts as a controlling factor during copolymerization of AAm/NaAc polyelectrolytes. Kabanov et al. did pioneering work in this respect and proposed that ion pairing affects the reactivities of ionizable monomers.¹¹ They related an increase in polymerization rate, observed upon adding salts, to ion pairing between the growing radicals and the counterions from the added salt, which diminished the electrostatic repulsions between like charged species at the reaction site. Paril et al. also studied the effect of IS on the rate for the AAm/AAC system at different AAc feed contents.¹² At low IS, they observed a reduction in the rate by introducing more AAc in the feed. They related this behavior to the stronger electrostatic repulsion upon increasing the AAc content, which made the polymerization slower. At high IS, on the other hand, they could not observe any specific trend between AAc content and copolymerization rate. However, it should be mentioned that in their study there were two variables affecting the system, namely, the AAc mole fraction in the feed and the total monomer concentration. Hence, the total monomer concentration varied at constant IS (both at low and high levels), which made it complicated to distinguish between the effects of these variables. Moreover, salt had been used in the carrier solvent, but not for maintaining IS constant between runs.

The reactivity ratios of monomers and radical species in copolymerization are also expected to change depending on the makeup of the reaction medium, since monomers, radicals and the resulting polymer chains may be ionized to varying extents. Ponratnam and Kapur observed an increase in reactivity ratios of AAc and AAm at pH = 4 by adding NaCl.⁵ They attributed this change to the partial neutralization of the ionic charges on the ionizable monomer, which caused in turn a faster addition of monomer units to the radicals. At pH = 6, adding 1M NaCl caused a slight decrease in r_{AAc} while the r_{AAm} remained constant. On the other hand, Kurenkov et al. noticed that r_{AAc} and r_{AAm} increased and decreased, respectively, after adding NaCl to the reaction at pH = 10.¹³ Paril et al. observed an increase in both reactivity ratios of AAc and AAm at pH = 3 but at higher

IS.¹² As mentioned before, this can also be caused by different total monomer concentrations in these studies, since the total monomer concentration varied as well. The effect of added salt is not unique to the AAm/AAC system. McCormick and Salazar examined the copolymerization of AAm and sodium 3-acrylamido-3-methylbutanoate (NaAMB) and found that the reactivity ratio of AAm decreased with adding 1M salt solution to the copolymerization, whereas the reactivity ratio of the charged monomer (NaAMB) increased.⁹

Therefore, a review of the relevant literature has revealed that, despite the importance of controlling the IS of this polyelectrolyte system, there is no systematic study of the effect of IS on the reaction kinetics of AAm/NaAc copolymerization. In addition, as explained earlier, in the few existing studies, the experimental observations are rather contradictory (both on polymerization kinetics and monomer reactivity ratios) with respect to the effects of this factor.

In a previous article, a systematic approach was applied to obtain more reliable reactivity ratios for AAm/AAC copolymerization by carrying out independently replicated polymerizations over the full conversion range.² Our initial studies targeted the case where the IS was variable (but known) for the different copolymerization runs, in order to be able to compare the estimated reactivity ratios of the system with literature values. The scope of this article is to study the effect of IS on the kinetics of AAm/NaAc copolymerizations at a chosen pH. In doing so, the experimental conditions for pH, temperature, total monomer concentration, and initiator concentration were the same for all the experiments. This level of control over these factors allowed us to investigate the effect of IS, without any interactions with other factors interfering into the picture. The IS was varied by changing the proportion of NaAc in the feed composition and also by adding NaCl into the reaction solution. First, the system was studied at constant IS by incorporating salt in the reaction recipe. Subsequently, the effect of having variable but controlled IS on the copolymerization system was studied. To our knowledge, there have been no other attempts to clarify the effect of IS as a single factor on the copolymerization kinetics of AAm/AAC (with AAc in the form of NaAc) so far.

EXPERIMENTAL

Materials

AAm (electrophoresis grade, $\geq 99\%$), AAc (99%), 4,4'-azo-bis-(4-cyano valeric acid), hydroquinone, and sodium hydroxide were purchased from Sigma-Aldrich. Water was Millipore quality ($18 \text{ M}\Omega \text{ cm}^{-1}$) and methanol was ACS grade from VWR. Nitrogen gas from Praxair (4.8 grade) was used for degassing of solutions. Sodium chloride was ACS grade from Merck.

Polymerization

AAc was purified by vacuum distillation at 30°C , in particular to remove diacrylic acid which may be produced during storage of AAc. Following this, primary monomer stock solutions with a total monomer concentration of 2M were prepared with the chosen monomer fractions. Then, measured amounts of AAm/AAC solutions were titrated with sodium hydroxide in order to adjust pH to 7 ± 0.2 . The degree of ionization of AAc was

Table I. Experimental Runs of AAm/NaAc Copolymerization at Various $f_{0\text{AAm}}$ and IS

Run #	$f_{0\text{AAm}}^a$	IS (M)	NaCl (M)
1	0.1	0.898	0
2	0.1	1.078	0.181
3	0.1	1.437	0.539
4	0.46	0.538	0
5	0.46	0.898	0.359
6	0.46	1.078	0.539
7	0.46	1.258	0.719
8	0.46	1.437	0.898

$f_{0\text{AAm}}$: initial mole fraction of AAm in the feed.

about 0.998. Therefore, AAc was fully converted to sodium acrylate (NaAc) in the system. After adding the 4,4'-azo-bis-(4-cyano valeric acid) initiator (final concentration of 0.004M) to the solution, the solution was further diluted with high purity water to achieve a total monomer concentration of 1M. Subsequently, measured amounts of sodium chloride were added, as needed, to set the IS of the solutions to the desired level.

The AAm monomer proportions in the feed solutions were $f_{0\text{AAm}} = 0.1$ and 0.46. These feed mole fractions were determined as optimal values (for the specific reaction conditions) for reactivity ratio estimation based on an optimal design criterion as described elsewhere.² A summary of the experimental details in the copolymerization runs is given in Table I. In all the experiments all of the other factors (including pH and therefore degree of ionization of AAc, total monomer concentration (1M), initiator concentration, and temperature) were kept constant. Each run was independently replicated at least once.

The solutions were then purged with nitrogen gas for 120 min with a gas flow rate of 200 mL min⁻¹ and then ca. 20 mL portions were transferred to vials, fitted with crimped rubber seals, using the so-called cannula transfer method.²

For the polymerization, the vials were put in a temperature controlled water shaker-bath (Grant, OLS200) at 40°C and 100 rpm. They were removed at specific time intervals and chilled in an ice bath. A few drops (0.5 mL) of inhibitor solution were quickly syringed into the vials to stop any further polymerization. Polymer products were then isolated by precipitation from a 10-fold excess of methanol.

Characterization

For determining monomer conversion, gravimetry was used. After precipitation, the polymer products were filtered (paper filter grade number 41, Whatman) and put in a vacuum oven at 50°C until they reached constant weight. Monomer conversions were determined as polymer mass over initial monomer mass. Elemental analysis (CHNS, Vario Micro Cube, Elementar) was used to measure the C, H, and N content of the samples. Copolymer composition was subsequently calculated based on the percentages of the C and N elements only (in order to

remove the effect of residual water in the samples which causes variability in the percentage of H).

The mass of NaAc (since AAc exists as sodium acrylate, having been neutralized with sodium hydroxide) plus AAm monomer was considered as the reactant mass in conversion calculations. The mass of sodium in the product was deduced from the polymer mass based on elemental analysis results. The reliability of Na mass calculations was independently checked for selected samples using inductively coupled plasma (ICP) analysis (Prodigy Radial ICP-OES by Teledyne-Leeman). It is worth mentioning that in experiments where various amounts of sodium hydroxide base and sodium chloride salt are added to the reaction mixture to control the pH and IS levels, respectively, it is crucial to consider the mass of the sodium ions in the calculations. Not doing so will introduce error and bias the results considerably. This is something that is usually neglected in the literature, although it should be routinely considered and discussed.

RESULTS AND DISCUSSION

Constant IS: Reactivity Ratios for Copolymerization at $f_{0\text{AAm}} = 0.46$

In a previous study that determined reactivity ratios for AAm/AAc at pH = 7 and total monomer concentration of 1M, IS was allowed to vary between runs based on the fraction of AAc in the feed composition.² In other words, since the two comonomer feeds ($f_{0\text{AAm}} = 0.1$ and $f_{0\text{AAm}} = 0.46$) used for reactivity ratio estimation had different levels of neutralized AAc, IS was not constant for the different feeds (Runs # 1 and 4 in Table I). A varying IS level represents the typical case in the literature. Most (if not all) of the reported reactivity ratio values in the literature have been calculated based on a “floating” IS. The broader study reported herein was undertaken to examine effects on estimated reactivity ratios caused by varying IS, at the same pH level, by adding various amounts of NaCl to the copolymerization solutions. But first the reactivity ratio estimation under constant IS will be considered.

On the basis of the IS data presented in Table I, NaCl was added to the solution at $f_{0\text{AAm}} = 0.46$ to give a concentration equal to 0.359M, in order to bring its IS level from 0.538 (Run # 4) to 0.898 (Run # 5), so that runs 1 and 5 had the same IS. Then, copolymerizations were conducted at the conditions outlined over the whole conversion range and cumulative copolymer compositions were determined. Figure 1 shows the cumulative copolymer composition of AAm, cum F_{AAm} , determined by elemental analysis versus conversion for $f_{0\text{AAm}} = 0.46$ at two IS levels (with independent replicates). It can be seen that incorporating 0.359M of NaCl leads to a slight decrease in the cumulative AAm copolymer composition, and hence a slight increase in NaAc incorporation.

On the basis of the cumulative copolymer compositions (cum F_{AAm}) and conversion results from Figure 1, reactivity ratios were estimated for runs 1 and 4 (variable IS) and runs 1 and 5 (constant IS). Figure 2 shows both point estimates for these reactivity ratios and the corresponding 95% joint confidence regions (JCRs). The reactivity ratio estimation was done based

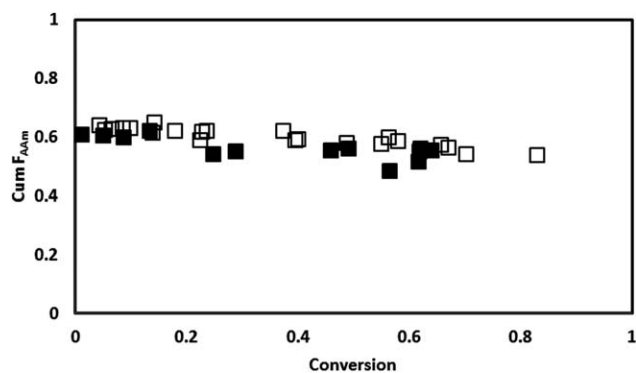


Figure 1. Cumulative copolymer composition of AAm versus conversion for $f_{0AAm} = 0.46$ (□ Run 4; ■ Run 5).

on the well-established error-in-variables-model (EVM) algorithm, where all the measurements (such as initial feed composition, conversion, or cumulative copolymer composition) are considered to have error.^{14,15} A recently described direct numerical integration (DNI) approach was employed in order to estimate the parameters over the whole conversion trajectory and gain complete process information (i.e., reactivity ratio estimation was not based solely on low conversion data, thus ignoring valuable process information from moderate to high conversion levels).¹⁶ More details on the estimation aspects of reactivity ratios can be found elsewhere.² JCRs in Figure 2 act as measures of the uncertainty (variability) related to the parameter estimates. A larger JCR denotes a higher variance and therefore higher variability in the system. Figure 2 makes several points. The error levels for the two sets of runs are almost identical (JCRs have about the same area), which is an indirect confirmation of the consistency of the experimental procedures and data collection. The JCRs demonstrate almost no covariance (no correlation) between the estimates (otherwise the obtained ellipses would be more inclined, with a positive or negative slope), which is another good feature of the estimation. Finally, one can see that the reactivity ratio value for r_{NaAc} has remained almost the same, while that for r_{AAm} has shifted to lower values (from a point estimate of 1.33 to 1.06), when IS stayed constant at a higher level (0.898). Of course, one could argue that the observed drop in the r_{AAm} value might be due to experimental

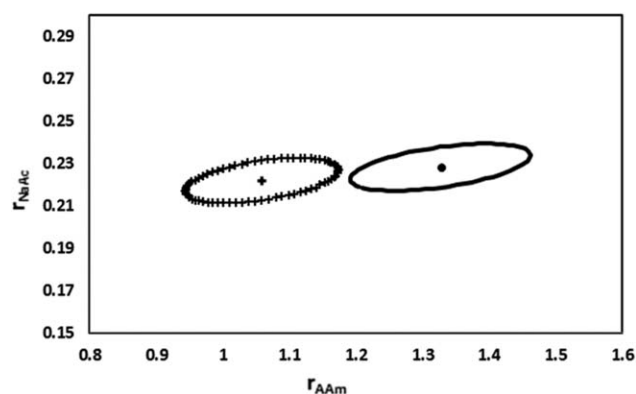


Figure 2. Reactivity ratios at variable and constant IS, (*,—) Runs (1, 4); (+, +++) Runs (1, 5).

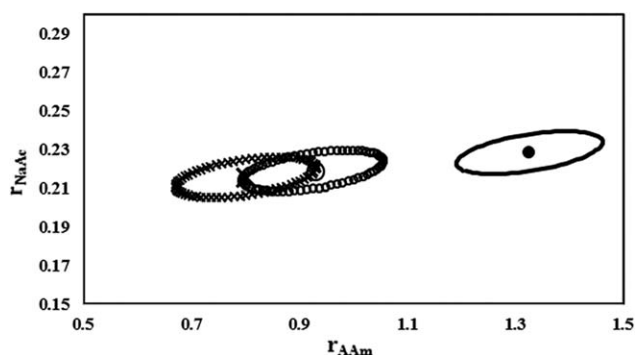


Figure 3. Reactivity ratio point estimates and JCRs for different IS levels in AAm/NaAc copolymerization. From right to left JCR: (*,—) Runs (1, 4); (○,○○) Runs (1, 6); (×,×××) Run (1, 8).

error, i.e., an experimental artifact. Therefore, the experiments were replicated independently and the validity of the trend was confirmed. To check the consistency of the trend of the IS effect on r_{AAm} , and also confirm the fact that the observed drop in r_{AAm} is due to a mechanistic reason (effect of salt addition), the investigation was continued at higher salt levels.

Controlled Variable IS: Reactivity Ratios for Copolymerization at $f_{0AAm} = 0.46$

The previous results showed that changes in IS (while maintaining other polymerization factors constant), affect the reactivity ratio of AAm, through the change in cumulative copolymer composition at $f_{0AAm} = 0.46$. To check if this effect on copolymerization kinetics extends to higher IS, more runs were conducted with progressively higher levels of sodium chloride, namely, 0.539, 0.719, and 0.898M, added to the $f_{0AAm} = 0.46$ solution (runs 6, 7, and 8 of Table I). In these experiments, the IS was not constant between the two feed composition levels (i.e., $f_{0AAm} = 0.1$ and 0.46) that were used for reactivity ratio estimation. However, the IS value was known (controlled) in order to examine the effect of changing IS on the cumulative F_{AAm} and estimated reactivity ratios. The collected copolymer composition and conversion results were used to estimate reactivity ratios for the runs (as described in 3.1) and the final outcomes of the analysis are shown in Figure 3.

The JCR for runs (1, 7) was overlapping with that of runs (1, 6) and so it is not included in the figure. In addition, the JCR for runs (1, 5) was now omitted, since it was shown earlier in Figure 2. Table II presents a summary of the point estimates of the reactivity ratios.

Table II. Reactivity Ratios for Copolymerizations at $f_{0AAm} = 0.46$ at Various IS Levels

Run #	r_{AAm}	r_{NaAc}
(1, 4)	1.326	0.228
(1, 5)	1.058	0.222
(1, 6)	0.926	0.218
(1, 7)	0.912	0.217
(1, 8)	0.802	0.215

It can thus be concluded from Figure 3 that by adding more sodium chloride to the reaction solution, r_{NaAc} remained almost unchanged, whereas r_{AAM} decreased significantly. Furthermore, this confirmed the trend observed in Figure 2.

Regarding the shift in the reactivity ratio values of AAm ($r_{\text{AAM}} = r_1 = k_{11}/k_{12}$), the AAm homo-propagation rate constant, k_{11} , is likely insensitive to the addition of salt, since the AAm homo-propagation reaction depends only on the AAm monomer and its radical, which are both uncharged at pH = 7. Hence, the drop in the r_{AAM} value must be due to changes (increases) in the value of the cross-propagation rate constant, k_{12} (AAm radical with NaAc monomer). This term should have increased significantly upon adding more salt to the reaction solution. To explain this, there must be changes in the nature of the overall charges of the polyelectrolyte chains. It is expected that without adding salt, the polyelectrolyte chains containing acrylate anions are more extended because of charge–charge repulsion between anionically charged groups along the chain, as is normal for polyelectrolyte solutions.¹⁷ In addition, there is a relatively low degree of shielding between the negative charges of the anionic acrylate repeat units in the copolymer chains and the free acrylate monomer. In the case with no added NaCl, with respect to runs (1, 4), there is a greater chance of repulsive interactions between unshielded negative charges, which makes the overall chance of reactive interactions for AAm lower. Hence, with added salt, the opposite will happen, and the cross-propagation rate constant will have the tendency to increase, thus causing a decrease in r_{AAM} .

Incorporating simple electrolytes (such as salts) to the aqueous solution makes the polymer chains to contract to denser random coil structures, since the repulsion interactions between acrylate groups are diminished.¹⁷ In other words, in polyelectrolyte solutions containing salt, the random coil structure of the copolymer chain is adopted because of the negative charge shielding of the acrylate anions by salt cations. This ion pairing increases the chance of the cross-propagation reaction because the degree of repulsion is diminished between the radical chain and the monomer, which makes the interaction of a growing radical ending in AAm radical with acrylate monomer more probable.

The most interesting observation from Figure 3 and Table II was that initially r_{AAM} was greater than unity and r_{NaAc} below unity, whereas after exceeding a certain amount of salt (and hence IS level) in copolymerizations at $f_{0\text{AAM}} = 0.46$, both reactivity ratios became less than unity. This represents a significant change in copolymerization behavior, as the system now, with both reactivity ratios below unity, is exhibiting potential azeotropic behavior. To confirm the reliability of the estimated reactivity ratios and the azeotropic behavior, the reactivity ratios for these runs were employed and the feed composition corresponding to the azeotropic point was calculated. For azeotropic conditions, f_1 in the feed should equal the corresponding mole fraction of monomer 1 in the copolymer, and therefore the cumulative copolymer composition should remain almost constant (within experimental error) with conversion. Based on the azeotropic runs of Table II, the suggested mole fraction for AAm in the feed was in the range of 0.79–0.91, so the average

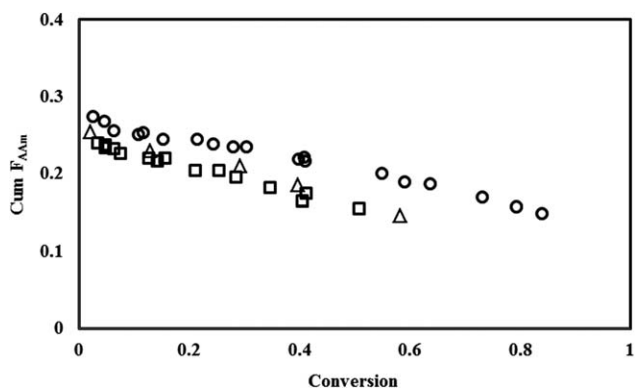


Figure 4. Cumulative copolymer composition versus conversion for AAm/NaAc at $f_{0\text{AAM}} = 0.1$ (○ Run 1; △ Run 2; □ Run 3).

value of 0.85 was considered. Therefore, another copolymerization was conducted to confirm this with a high level of AAm at $f_{0\text{AAM}} = 0.85$. The collected 11 conversion and cumulative copolymer composition data points (not shown here in their entirety for the sake of brevity) gave an average copolymer composition of 0.86 with a standard deviation of 0.013, which was very close (within typical experimental error) to the initial AAm mole fraction in the feed. This is characteristic of azeotropic behavior, thus confirming the validity of the reactivity ratio estimates.

Constant IS: Reactivity Ratios for Copolymerization at $f_{0\text{AAM}} = 0.1$

To check the effect of IS on the other optimal feed composition, $f_{0\text{AAM}} = 0.1$, experiments were run at two levels of added NaCl, namely, 0.181 and 0.539M (runs 2 and 3 of Table I) in order to obtain the same IS as runs 6 and 8, respectively. Cumulative copolymer composition of AAm versus conversion data for these two salt levels (runs 2 and 3 of Table I) were obtained and the results are compared with those for the polymerization without adding salt (run 1 of Table I) in Figure 4.

As can be inferred from the plot, the added salt in the copolymerizations with $f_{0\text{AAM}} = 0.1$ resulted in less incorporation of AAm in the copolymer. This again suggests that incorporating salt and consequently increasing IS, shields the negative charge interactions of acrylate anions and makes the system electrostatically more stable, which results in the presence of more NaAc (less AAm) units in the copolymer chain. This trend agrees well with what was seen for the experiments with $f_{0\text{AAM}} = 0.46$. It is also in agreement with trends of copolymer composition versus concentration of added salts described by McCormick and Salazar for copolymerization of AAm and sodium 3-acrylamido-3-methylbutanoate.⁹

Using the copolymer composition and conversion results, reactivity ratios were estimated for runs (2, 6) and (3, 8) of Table I, which had the same IS between two feed compositions (i.e., between $f_{0\text{AAM}} = 0.1$ and 0.46). Point estimates and JCRs for the reactivity ratios of these runs are compared in Figure 5 with runs (1, 4), where there was no salt addition in the copolymerization. Table III also cites the point estimates of Figure 5.

Considering Figure 5 and Table III reveals that adding more salt to the solutions with higher NaAc content in the feed,

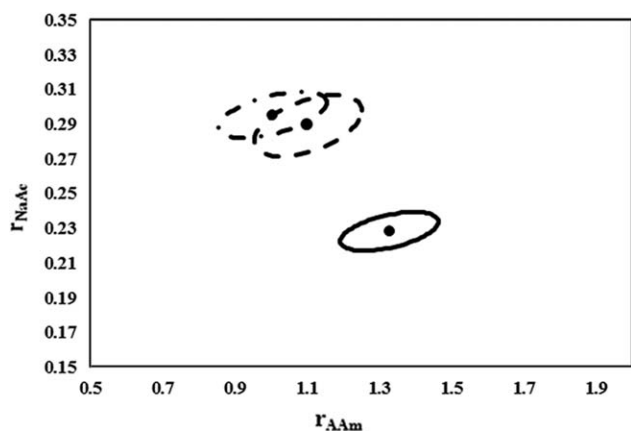


Figure 5. Reactivity ratio point estimates and JCRs. (•, —) Runs (1, 4); (•, - -) Runs (2, 6); (•, - . -) Runs (3, 8).

$f_{0AAm} = 0.1$, had more of an effect on the reactivity ratio of NaAc compared with the runs at lower NaAc content, $f_{0AAm} = 0.46$. This was expected since the NaAc addition was the preferred reaction, and so shielding by adding salt facilitated the homo-propagation of NaAc relative to cross-propagation and therefore increased r_{NaAc} . The decrease in r_{AAm} with salt addition is also consistent with earlier discussion.

Effect of IS on Copolymerization Rate

Besides the effect of IS on the monomer reactivity ratios, it has been observed that having different salt amounts in the aqueous solution, changes the overall copolymerization rate.^{11,12} Figure 6 shows monomer conversion versus reaction time profiles for the two cases with low and high IS at $f_{0AAm} = 0.46$ (runs 5 and 8). It can be seen from this figure that a higher salt level (0.898M NaCl compared with 0.359M) in the polyelectrolyte solution, made the copolymerization reaction faster, pointing again

Table III. Reactivity Ratios for Copolymerizations at $f_{0AAm} = 0.1$.

Run #	r_{AAm}	r_{NaAc}
(1, 4)	1.326	0.228
(2,6)	1.101	0.289
(3,8)	1.003	0.295

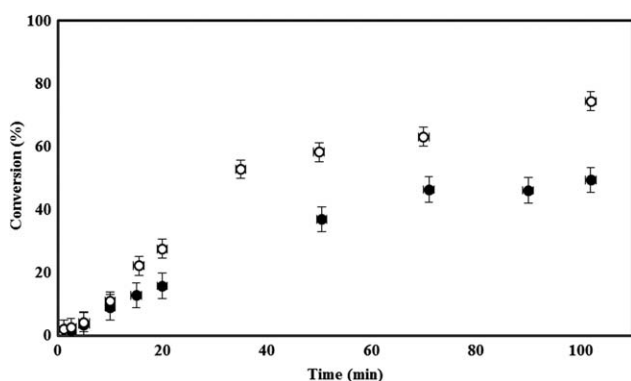


Figure 6. Conversion versus time profiles for copolymerizations at $f_{0AAm} = 0.46$; (•) Run 5; (○) Run 8.

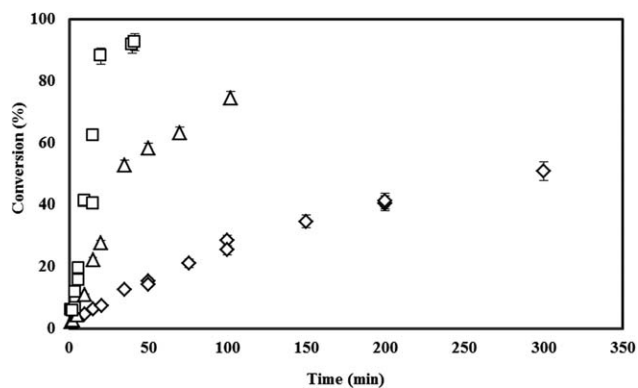


Figure 7. Conversion versus time profiles for AAm/NaAc copolymerization at constant IS (◇ run 3; △ run 8; □ run at $f_{0AAm} = 0.85$ and 1.288M salt).

towards the shielding effect of salt and less repulsion interactions between reacting species.

If IS is constant, though, having more NaAc content in the feed composition can cause a reduction in the overall copolymerization rate. Figure 7 compares the copolymerization rates of the runs with the same IS but different feed compositions (runs 3 and 8 of Table I). In addition, an extra copolymerization run was conducted at $f_{0AAm} = 0.85$ with 1.288M salt in order to reach the same IS as runs 3 and 8. Considering these rates at the same experimental conditions, including pH and IS, it is again observed that the rate for runs with higher NaAc is slower, due to the electrostatic repulsion between negatively charged reacting species. Effectively, Figures 6 and 7 represent a corroboration of the results and trends observed earlier.

CONCLUSIONS

The largely unstudied effect of ionic strength on monomer reactivity ratios and overall polymerization rate of the polyelectrolyte AAm/AAc (AAc in the form of sodium acrylate, NaAc) copolymer system was investigated experimentally. It has been shown that at various feed compositions, incorporating salt in the reaction solution, affects the monomer reactivity ratios as well as the copolymerization rate, by decreasing the electrostatic repulsions between the charged ions. It has also been shown that depending on the initial feed composition of the solution, the effect of ionic strength on reactivity ratios is different. By adding sodium chloride to the polymerization solution with initial feed composition of $f_{0AAm} = 0.46$, r_{NaAc} remains almost unchanged, whereas r_{AAm} decreases significantly, with a shift into azeotropic copolymerization. However, at copolymerizations with more NaAc in the feed, $f_{0AAm} = 0.1$, the effect on the reactivity ratio of NaAc is more obvious.

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