# Reactivity Ratios in Polyelectrolyte Copolymerization: Does Ionic Strength Play a Role?

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## Research Motivation

To investigate and clarify the largely unstudied effect of ionic strength on monomer reactivity ratios and copolymerization rates of acrylamide (AAm) and acrylic acid (AAc), in the form of sodium acrylate (NaAc), at a chosen pH.

## Experimental

**Materials**
- Acrylamide, AAm and Sodium acrylate, NaAc (Monomer)
- Sodium hydroxide (pH-controller)
- 4,4′-azo-bis-(4-cyano valeric acid), ACVA (Initiator)
- Hydroquinone (Inhibitor), Sodium chloride (salt)

**Estimation**
- Error-in-Variables Model (EVM) & Direct Numerical Integration (DNI) approach for estimating monomer reactivity ratios

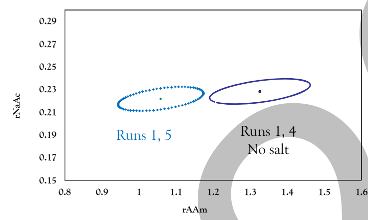
**Characterization**
- Gravimetry for monomer conversion
- Elemental analysis for copolymer composition
- Inductively coupled plasma (ICP) analysis for Na content

**Polymerization**
- Total monomer concentration = 1 M
- Temperature = 40 °C
- Solution pH = 7±0.2
- AAm monomer proportions in feed = 0.1, 0.46

| Run # | $f_{0AAm}$ | Ionic Strength (M) | Salt (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 |

## Ionic Strength & Reactivity Ratios

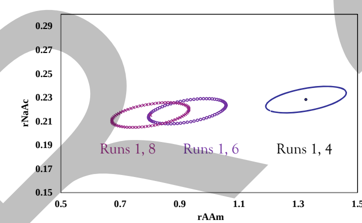
### *Copolymerization with Constant Ionic Strength at $f_{0AAm}$=0.46*




OBSERVATION
By keeping ionic strength constant:
$r_{NaAc}$ has remained almost the same,
$r_{AAm}$ has shifted to lower values.

REASONING
Without adding salt, the polyelectrolyte chains containing acrylate anions are more extended because of charge-charge repulsion between anionically charged groups along the chain.

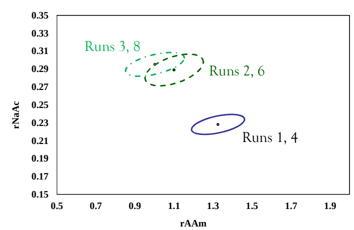
### *Copolymerization with Controlled but Variable Ionic Strength at $f_{0AAm}$=0.46*




OBSERVATION
By increasing ionic strength:
$r_{NaAc}$ has slightly shifted to lower values,
$r_{AAm}$ has noticeably shifted to lower values.

REASONING
Having more salt means greater chance of diminishing the repulsive interactions between unshielded negative charges & yielding denser random coil structure.

### *Copolymerization with Constant Ionic Strength at $f_{0AAm}$=0.1*

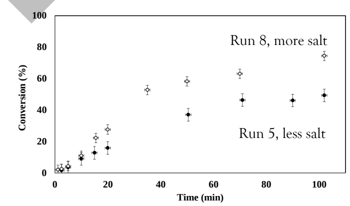



OBSERVATION
By increasing ionic strength:
$r_{NaAc}$ has shifted to higher values,
$r_{AAm}$ has shifted to lower values.

REASONING
Incorporating salt shields the negative charge interactions of acrylate anions, which results in higher reactivity for NaAc units.

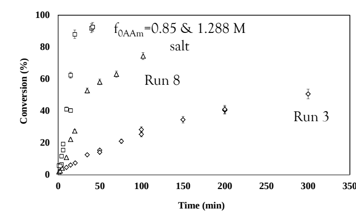
## Ionic Strength & Polymerization Rate

### *Variable Ionic Strength*




Higher salt level, faster copolymerization rate; due to the shielding effect of salt & less repulsion interactions between reacting species.

### *Constant Ionic Strength*




Higher NaAc in the feed composition, slower overall copolymerization rate; due to the electrostatic repulsion between negatively charged reacting species.

## Concluding Remarks

- ✓ Incorporating salt in the reaction solution, at various feed compositions, affects monomer reactivity ratios as well as the copolymerization rate, by decreasing the electrostatic repulsions between charged ions.
- ✓ Depending on the initial feed composition of the solution, the effect of ionic strength on reactivity ratios is different. By adding salt to the polymerization solution with initial feed composition of $f_{0AAm}$=0.46, $r_{NaAc}$ remains almost unchanged, whereas at $f_{0AAm}$=0.1, the effect on $r_{NaAc}$ is more obvious.