

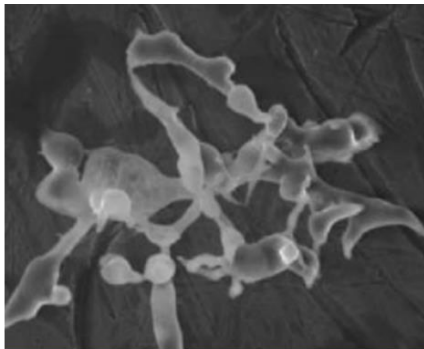
## **The influence of sulfide ion on viscosity of HPAM solution used in oil recovery and the concerning mechanisms**

**East China University of Science and Technology**

**Jinfeng Liu**

**21<sup>th</sup> July, 2016**

## Background of this research



### Classification

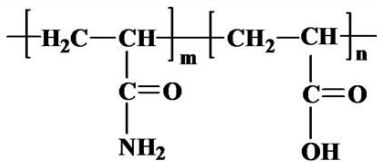
- Anionic / Cationic
- Nonionic
- Zwitterionic

### Properties

- $M_w$  :  $0.2-20 \times 10^6$  Da
- Hydrophilic, Good water solubility
- Flow property, Flocculation.....

### Applications

- Oil-displacing agent
- Regulator / stabilizer of drilling fluid
- Water treatment agent

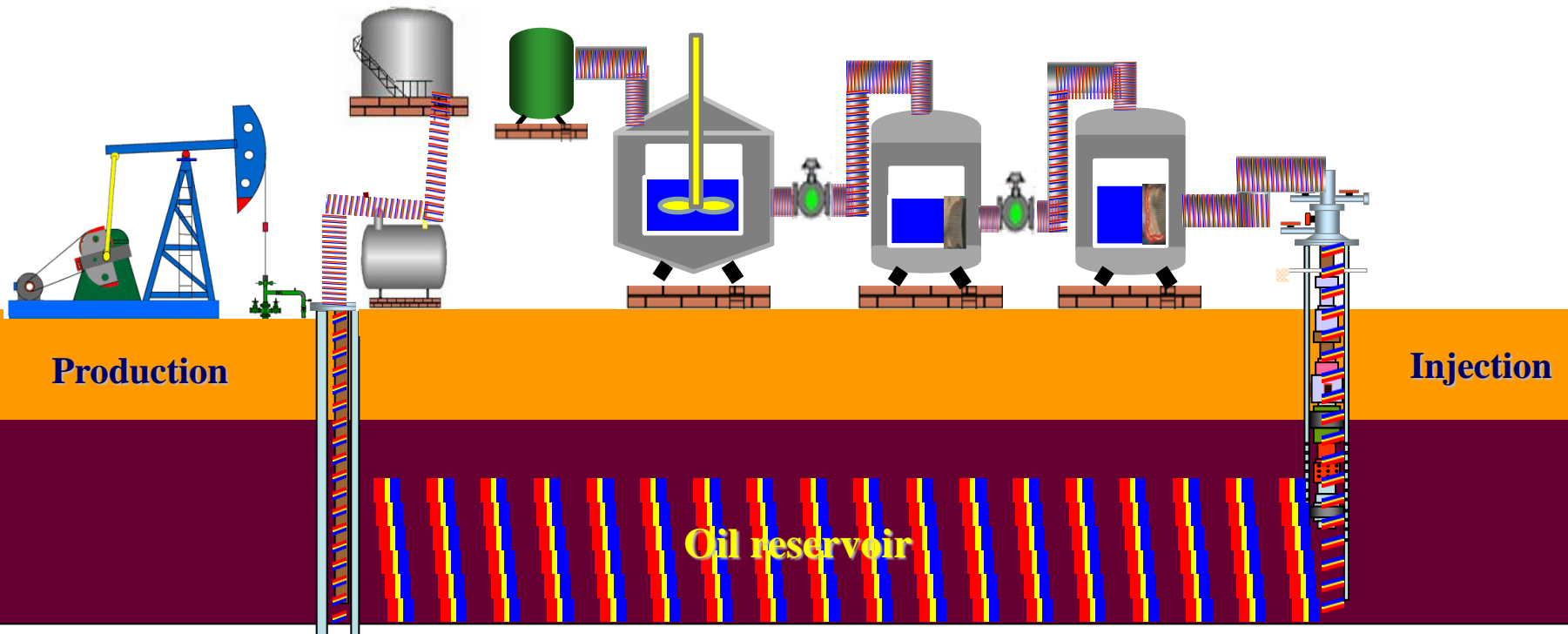


## The structure and property of HPAM

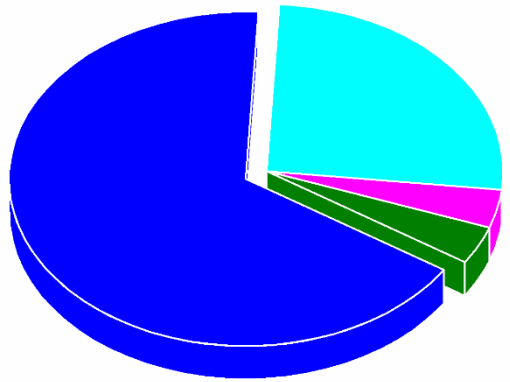
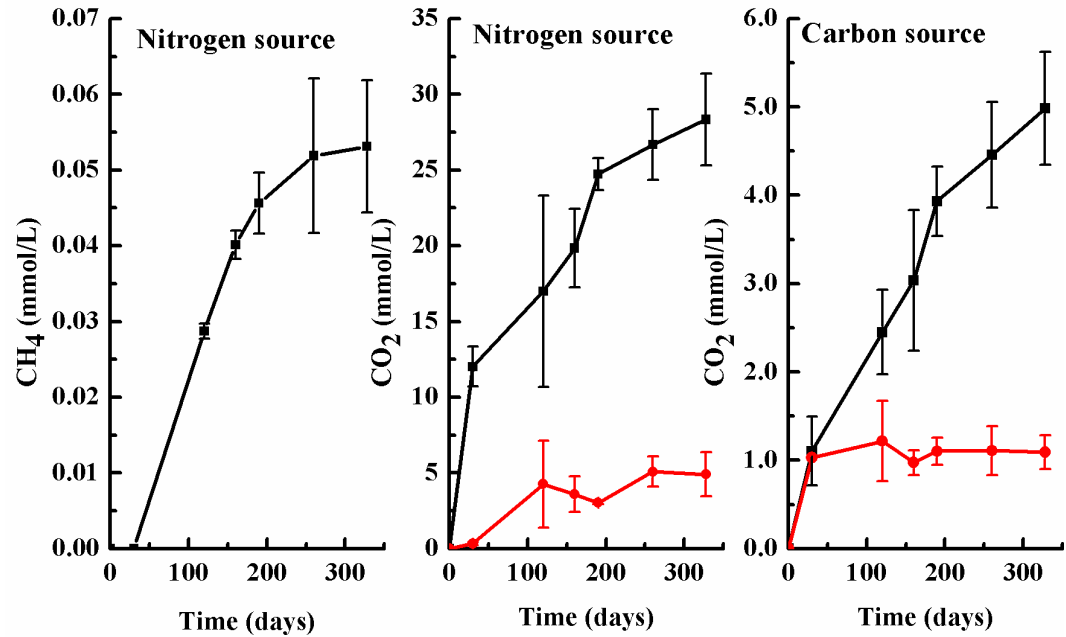
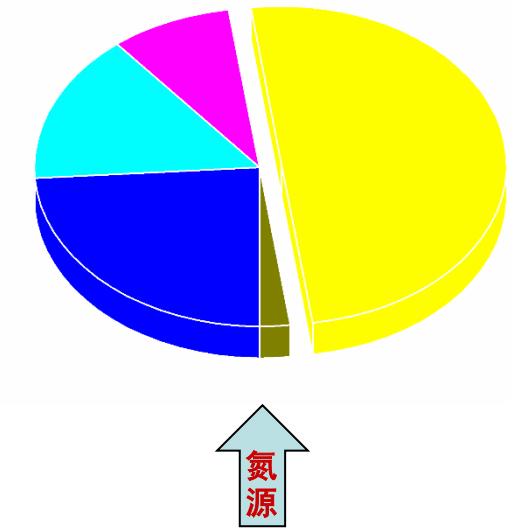
## Background of this research

★ Viscosity reduction negatively and notably influenced the HPAM flooding effect

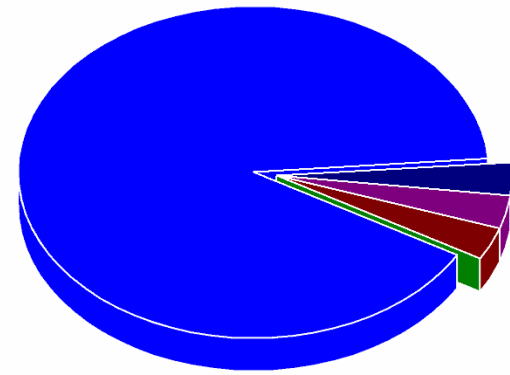
- Physical factors: pH, Temperature, Salinity, Shearing and etc
- Biological factors: Biodegradation ...



## Background of this research



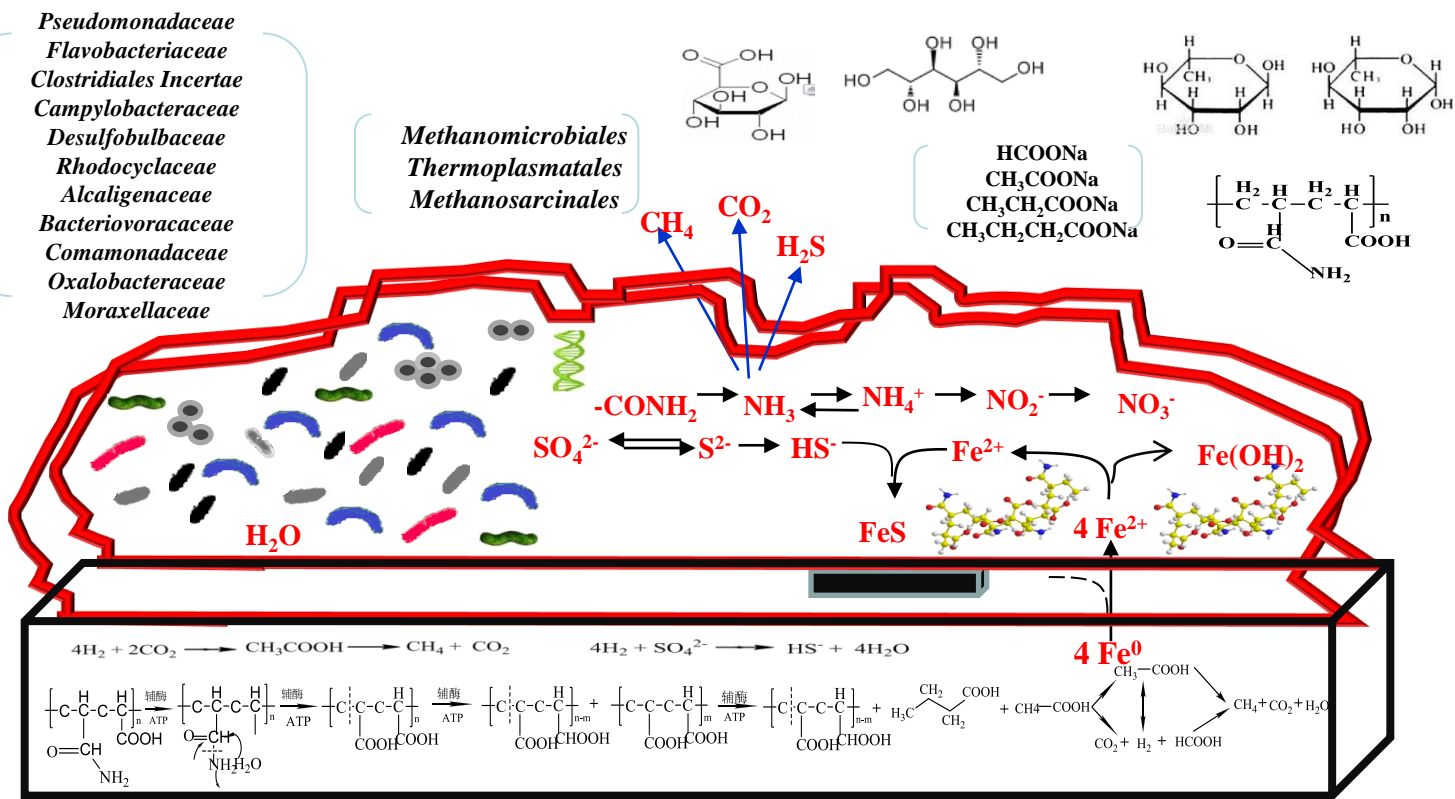
碳源



- *Proteobacteria*
- *Thermotogae*
- *Firmicutes*
- *Planctomycetes*
- *Deferribacteres*
- *Bacteroidetes*
- *Tenericutes*
- *Synergistetes*
- *unclassified*

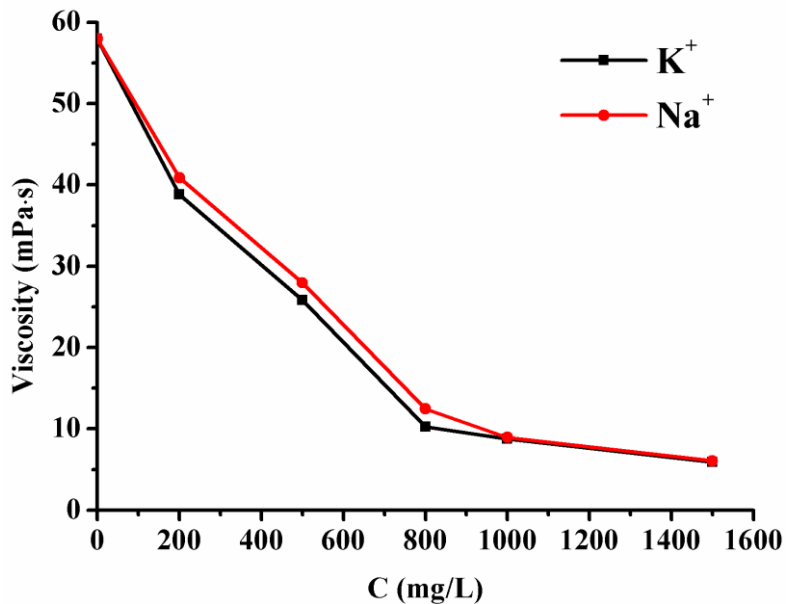
# Sulfide influence on HPAM viscosity and the concerning mechanism

## Background of this research

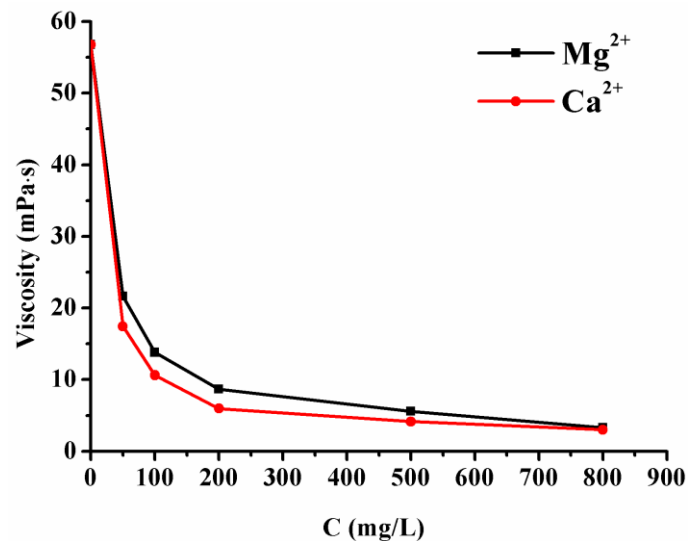


# Sulfide influence on HPAM viscosity and the concerning mechanism

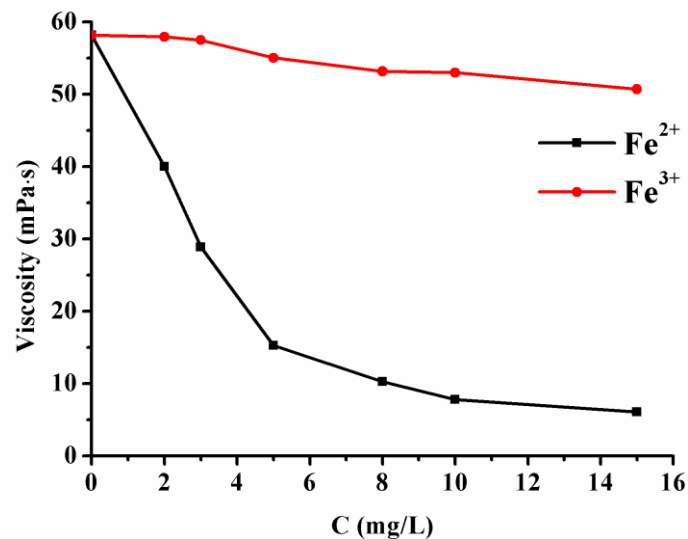
## Background of this research



Na<sup>+</sup> / K<sup>+</sup> effect on viscosity of HPAM solution



Mg<sup>2+</sup> / Ca<sup>2+</sup> effect on viscosity of HPAM solution



Fe<sup>2+</sup> / Fe<sup>3+</sup> effect on viscosity of HPAM solution

## Background of this research

Mechanical shear force exceeds the range of tolerance force of HPAM / **Well Characterised**

Viscosity decreases with increasing temperature. Dramatically under acidic conditions / **Well Characterised**

**Shearing**

**Ions**

**Tem & pH**

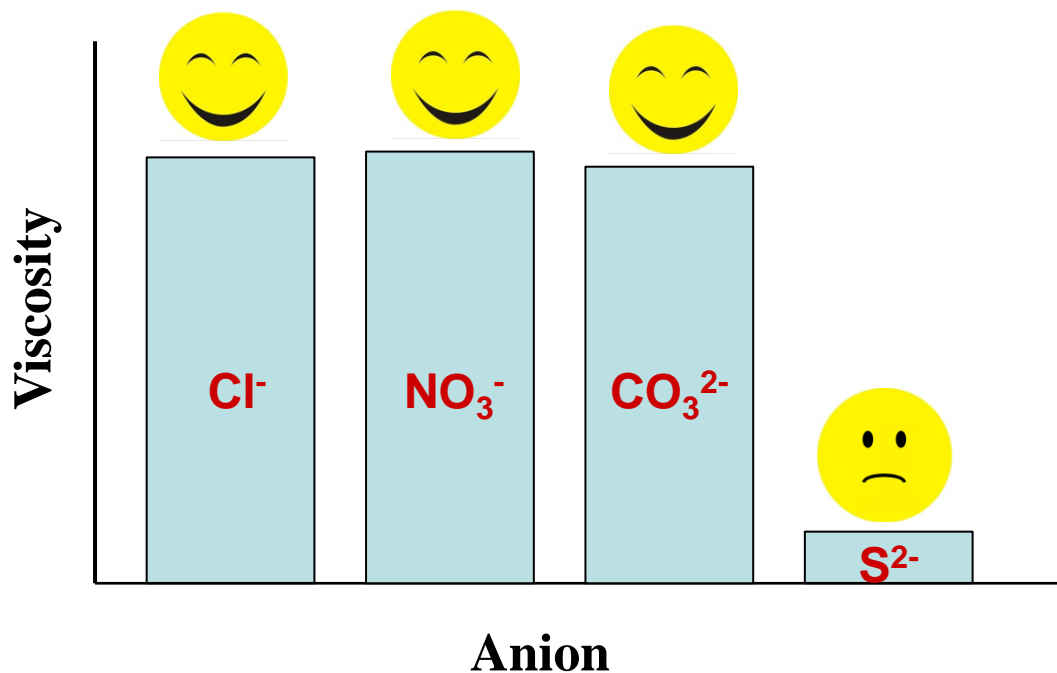
**Microorganisms**

The higher cation valence, the greater effect on the viscosity, / **Well Characterised**

Biodegradation reduces the viscosity via scission of HPAM backbone chain / **Characterised**

## Principal factors impacting on HPAM viscosity

## Background of this research

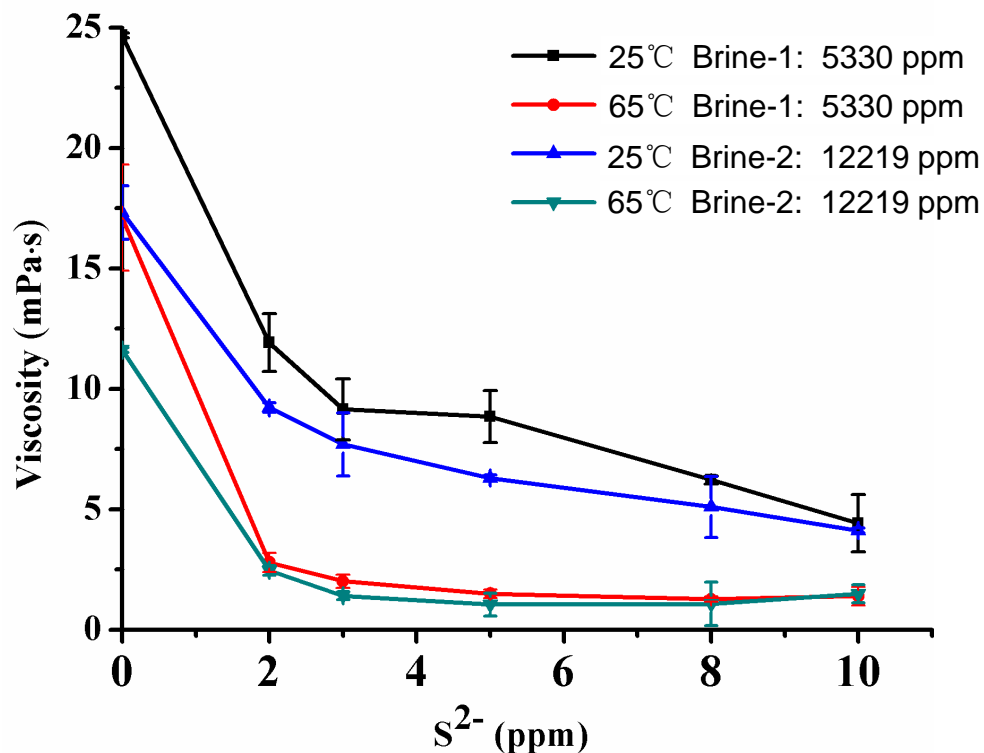


**Influence of  $\text{S}^{2-}$  on HPAM viscosity**



# Sulfide influence on HPAM viscosity and the concerning mechanism

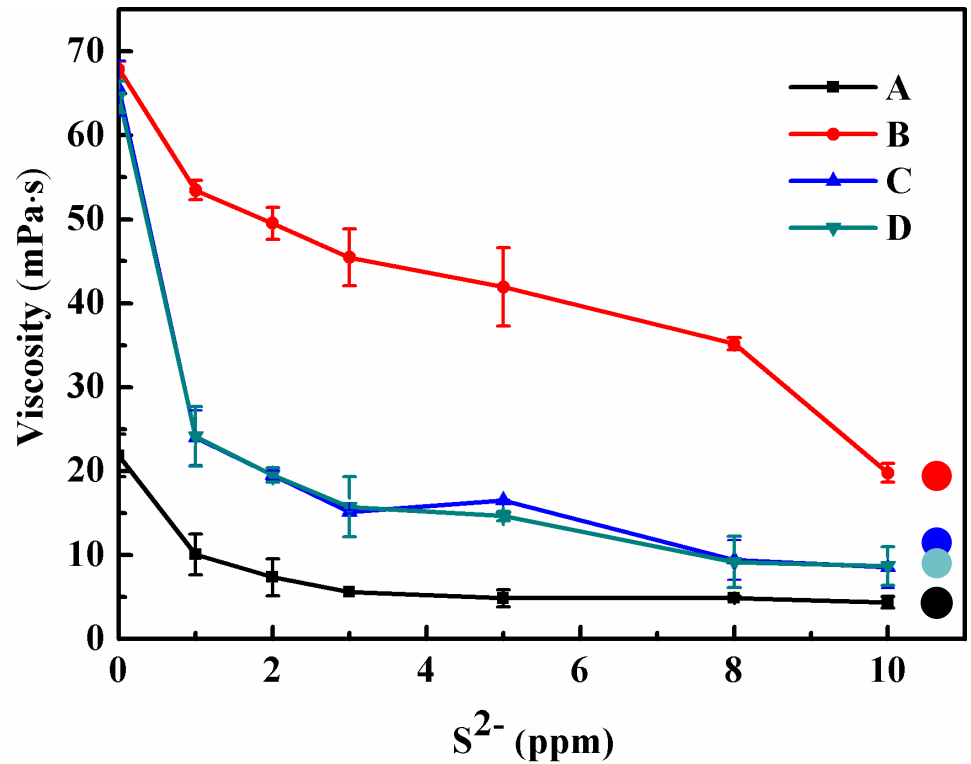
## The influence of sulfide ions on viscosity of HPAM solution



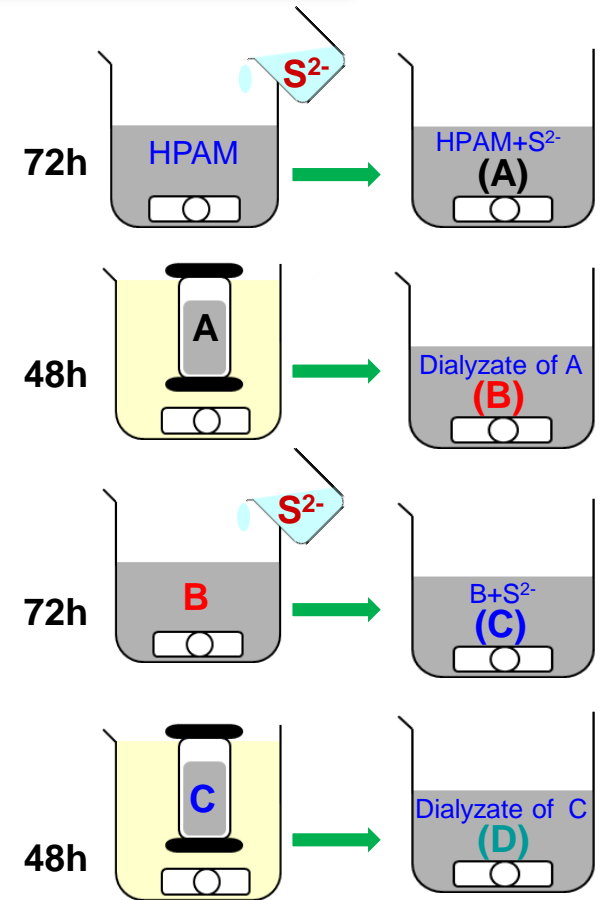
The effect of S<sup>2-</sup> on viscosity of HPAM solution prepared with simulated formation water

# Sulfide influence on HPAM viscosity and the concerning mechanism

## The influence of sulfide ions on viscosity of HPAM solution



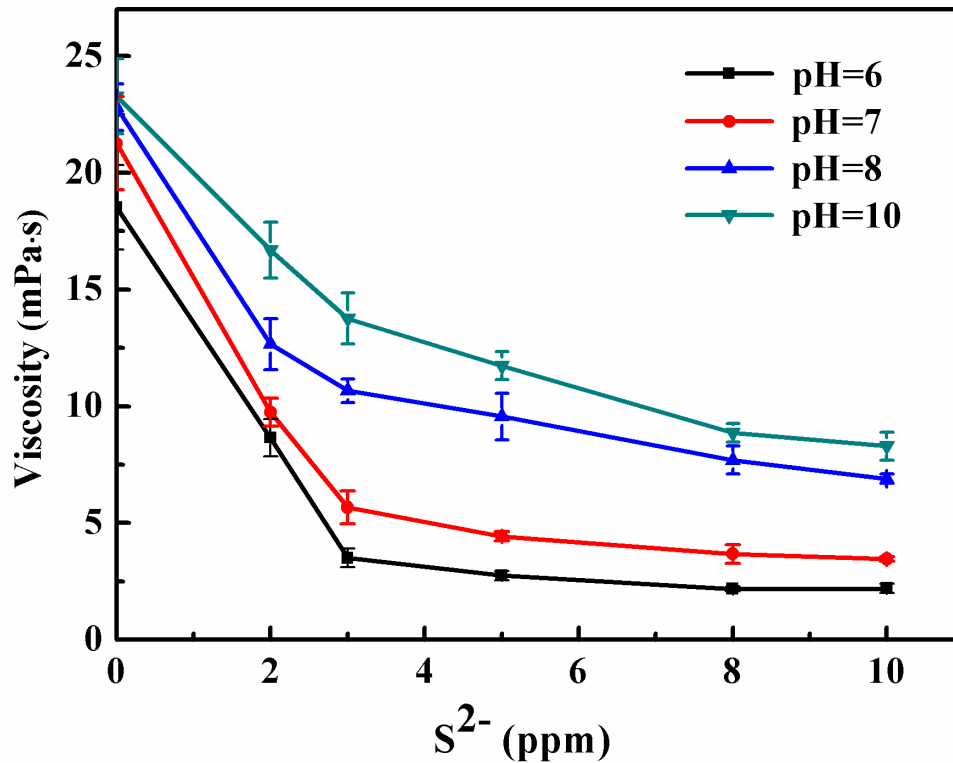
The viscosity of HPAM solution with different concentration of S<sup>2-</sup> before and after dialysis treatment



- A: Viscosity at 72 hrs after addition of S<sup>2-</sup>
- B: Viscosity of the 48 hrs dialysate from A
- C: Viscosity of B after addition of S<sup>2-</sup> for 72 hrs;
- D: Viscosity of the 48 hrs dialysate from C

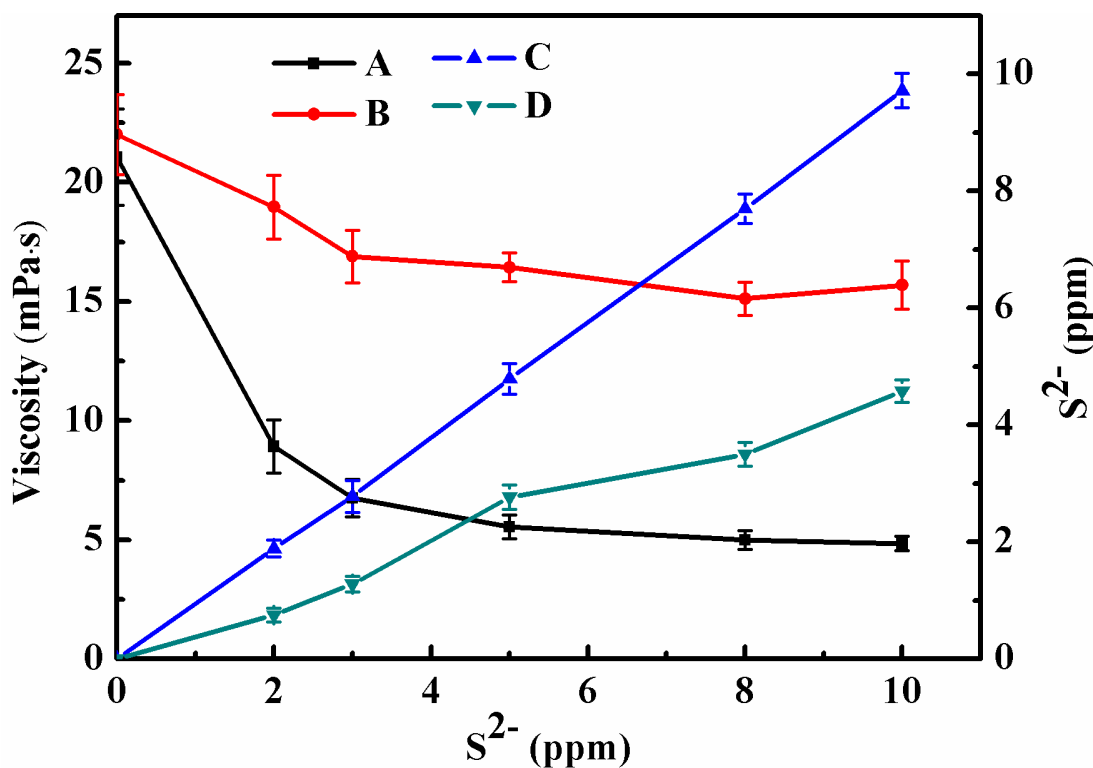
# Sulfide influence on HPAM viscosity and the concerning mechanism

The influence of sulfide ions on viscosity of HPAM solution



The viscosity of HPAM solution under different concentration of S<sup>2-</sup> and pH conditions

## The influence of sulfide ions on viscosity of HPAM solution

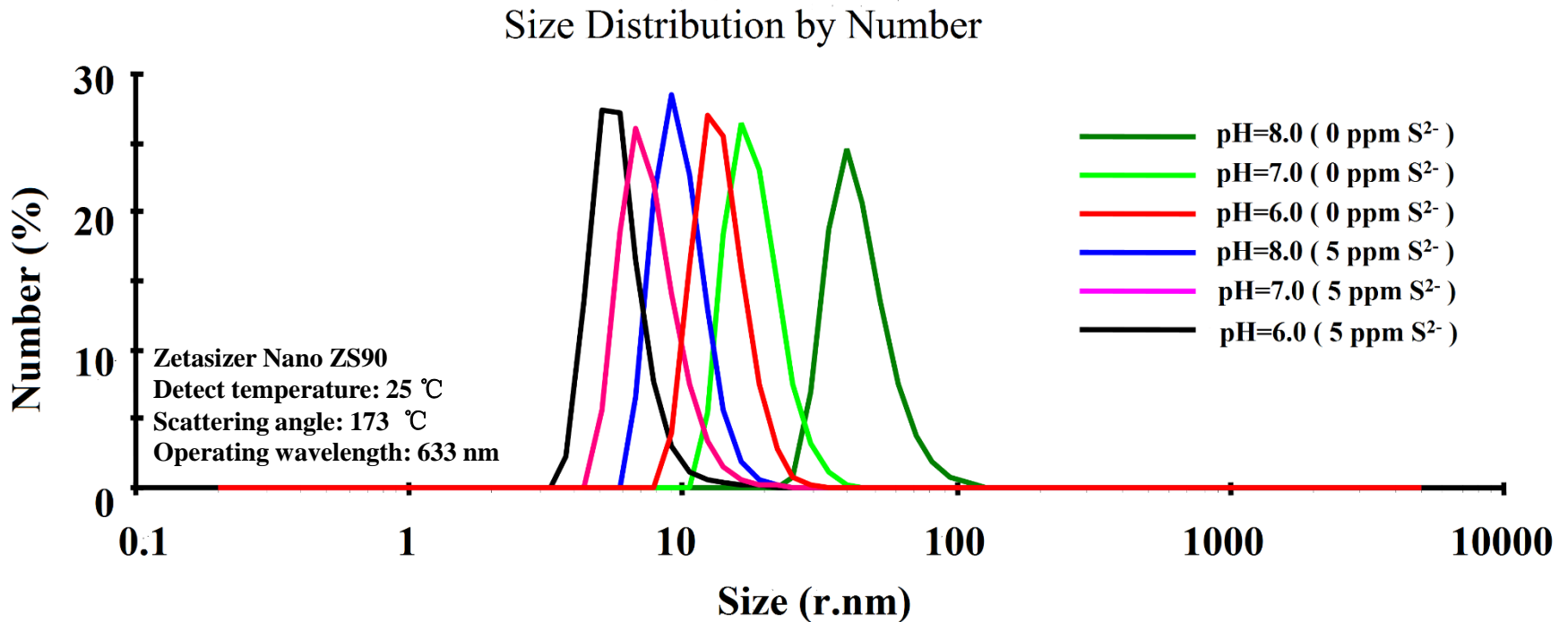


Stronger influence of S<sup>2-</sup> on viscosity of HPAM was observed under DO conditions than that without DO; So, this influence is proposed to be oxygen dependent.

A: Viscosity with S<sup>2-</sup> under DO conditions      D: S<sup>2-</sup> concentration under DO conditions  
 B: Viscosity with S<sup>2-</sup> under anoxic condition;      C: S<sup>2-</sup> concentration under oxygen-free conditions

**The viscosity of HPAM solution with different concentration of S<sup>2-</sup> with and without DO**

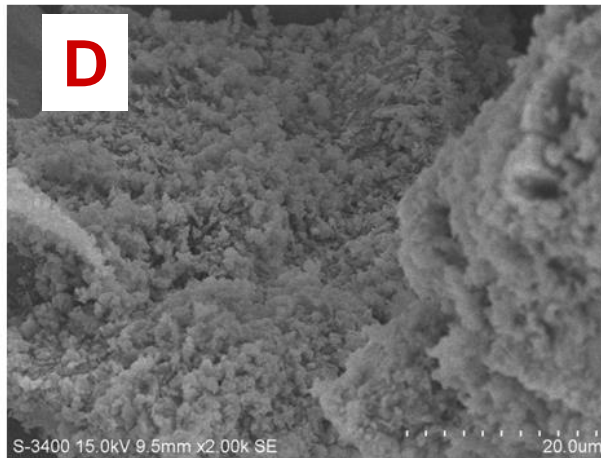
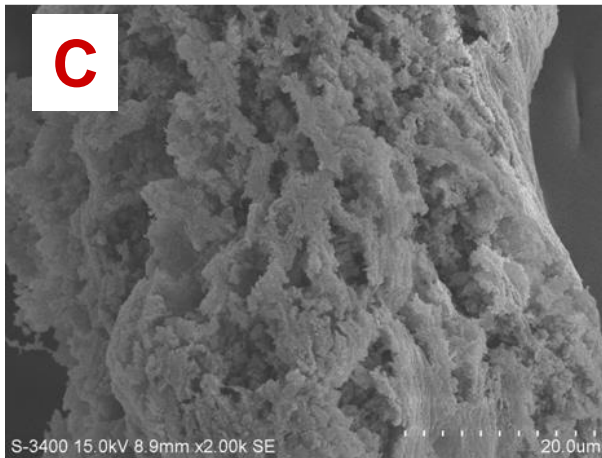
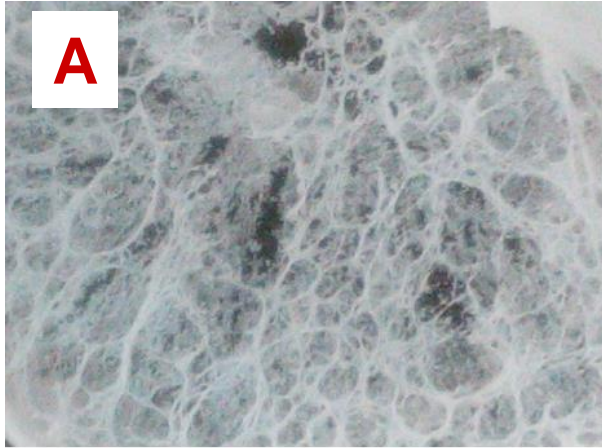
## The influence of sulfide ions on hydrodynamic radius of HPAM



The change in particle size of HPAM under different concentration of S<sup>2-</sup> and pH conditions

# Sulfide influence on HPAM viscosity and the concerning mechanism

## The influence of sulfide ions on microstructure of HPAM



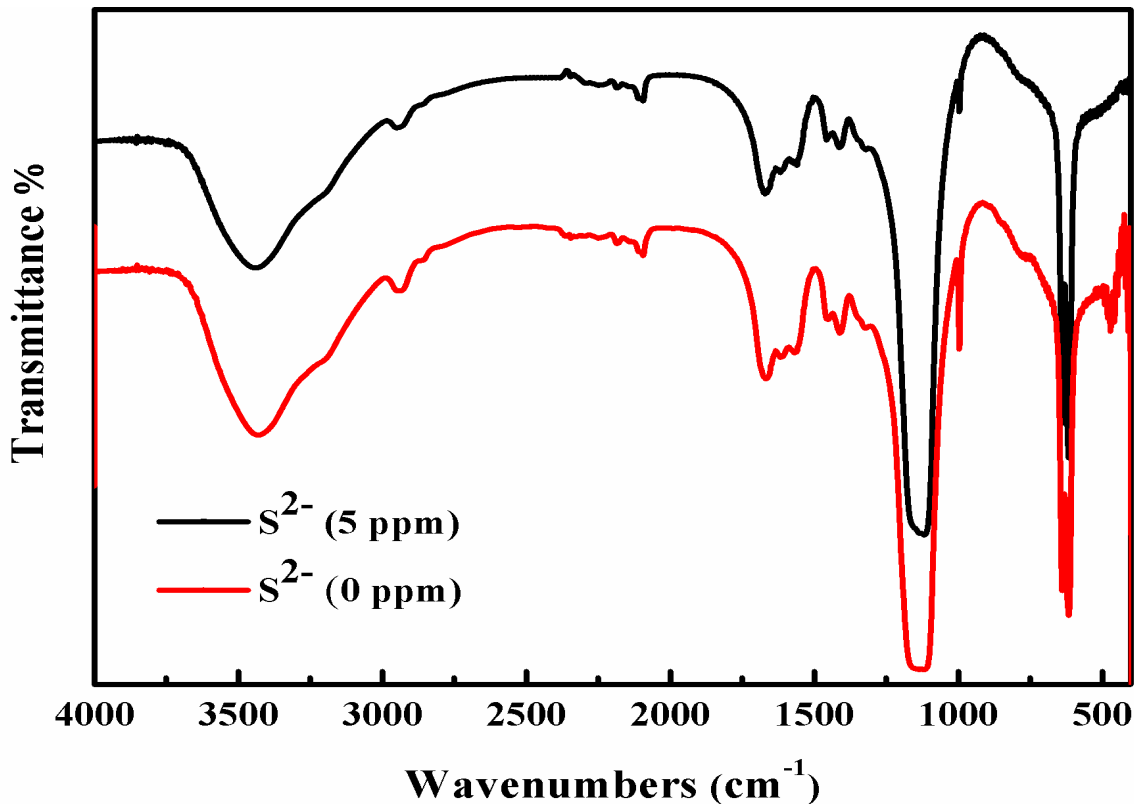
**A&C: 0 ppm  $S^{2-}$**   
**B&D: 5 ppm  $S^{2-}$**

Without  $S^{2-}$  (A and C), HPAM forms a network structure, resulting in high viscosity; while  $S^{2-}$  added (B and D), the network structure is significantly damaged, thus the viscosity be greatly reduced.

The micromorphology of HPAM

# Sulfide influence on HPAM viscosity and the concerning mechanism

## The influence of sulfide ions on the structure of HPAM



**N-H: 3100-3500  $\text{cm}^{-1}$**   
(stretching vibration)

**N-H: 1475  $\text{cm}^{-1}$**   
(bending vibration)

**C=O: 1615  $\text{cm}^{-1}$**   
(stretching vibration)

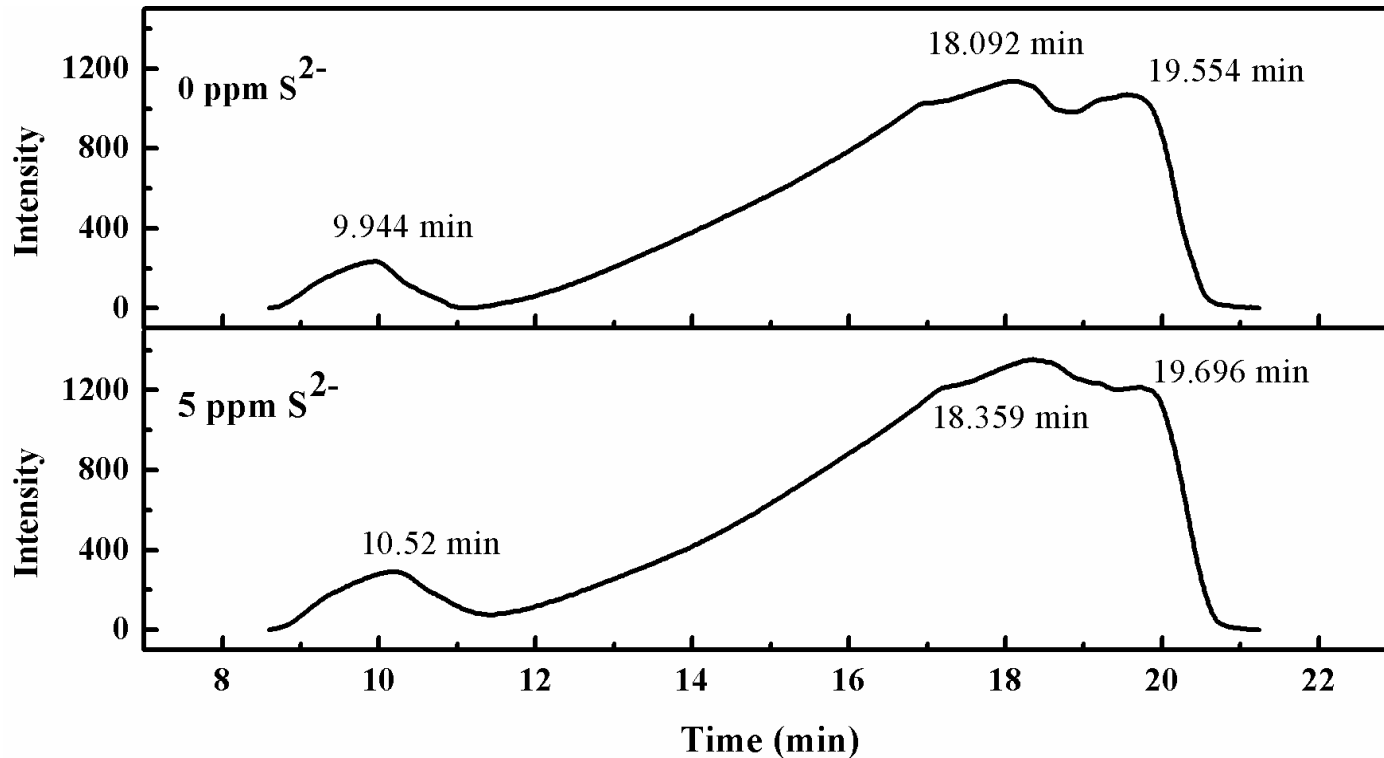
**C-N: 1415  $\text{cm}^{-1}$**   
(stretching vibration)

**C-O: 1130  $\text{cm}^{-1}$**   
(stretching vibration)

The FT-IR spectroscopy of HPAM before and after interaction with  $\text{S}^{2-}$

# Sulfide influence on HPAM viscosity and the concerning mechanism

## The influence of sulfide ions on Mw of HPAM

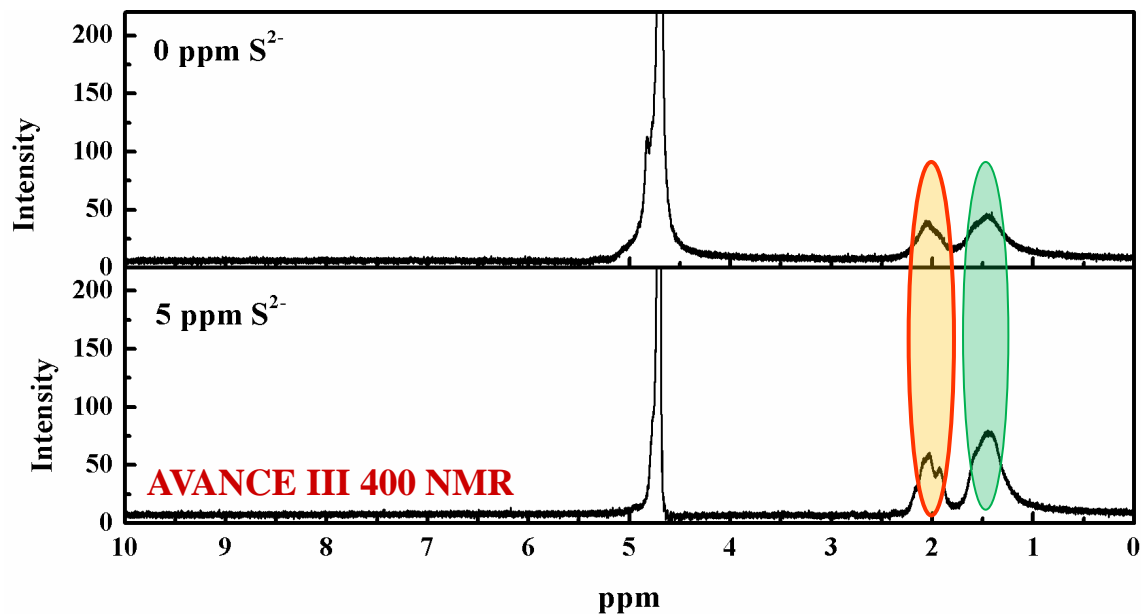
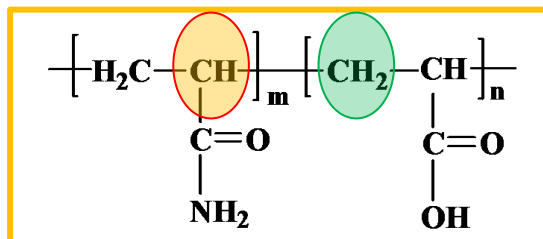


The GPC analysis of HPAM before and after interaction with  $S^{2-}$



# Sulfide influence on HPAM viscosity and the concerning mechanism

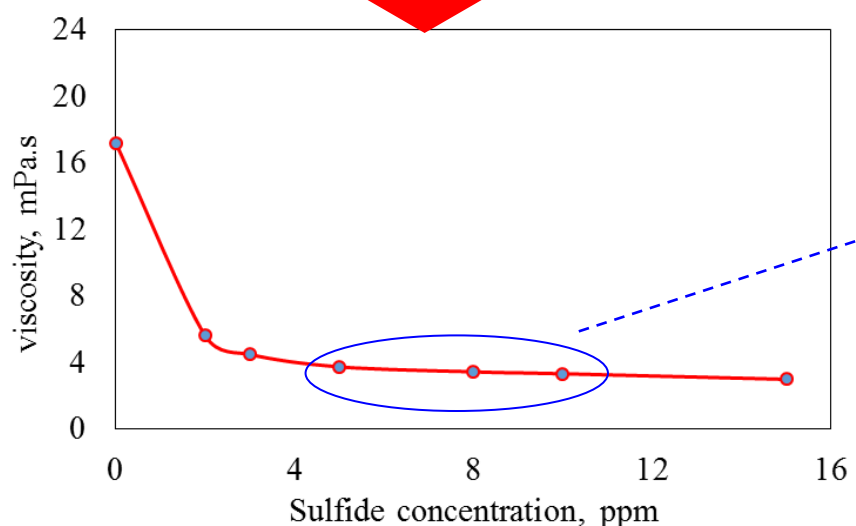
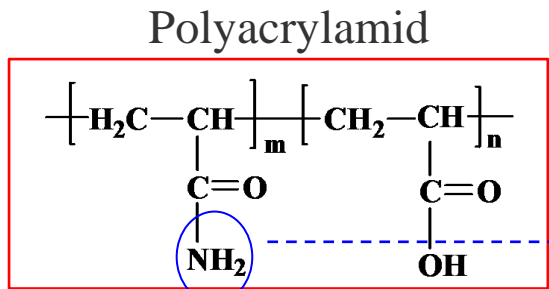
## The interaction site of sulfide ions and HPAM



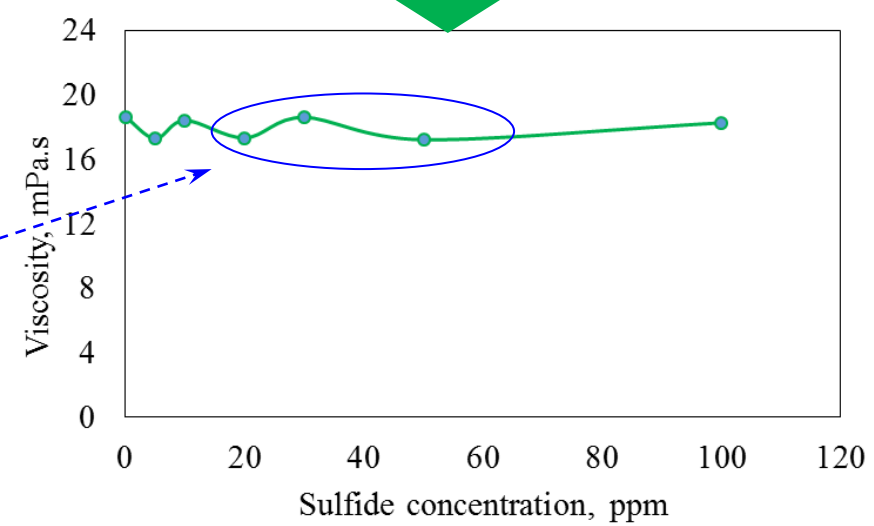
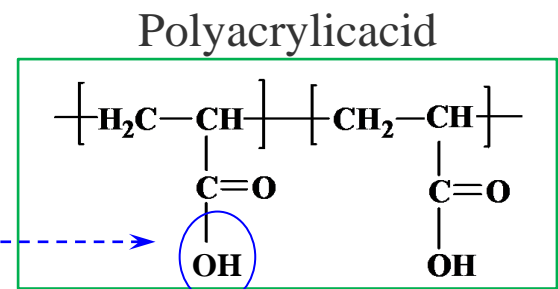
The  $^1\text{H}$  NMR before and after interaction with  $\text{S}^{2-}$

# Sulfide influence on HPAM viscosity and the concerning mechanism

## The interaction site of sulfide ions and HPAM



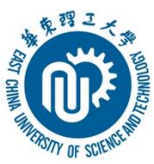
The viscosity of HPAM solution with different concentration of  $\text{S}^{2-}$  at pH =7



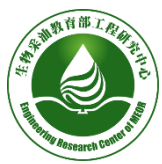
The viscosity of HPAAC solution with different concentration of  $\text{S}^{2-}$  at pH =7

## Summary

- The viscosity of HPAM solution is sensitive to cationic ions, the sensitivity is in this order as:  $\text{Fe}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ ; wherein,  $\text{Fe}^{2+}$  is the most distinguish one which can significantly reduce the viscosity of HPAM solution at a concentration of 5 mg/L.
- Under sufficient oxygen, the lower the pH and the higher the temperature, the more significant the influence of  $\text{S}^{2-}$  on viscosity of HPAM solution. However, under anaerobic conditions,  $\text{S}^{2-}$  shows no or not significant effect on the viscosity.
- $\text{S}^{2-}$  largely reduce the viscosity through destroying the network structure of HPAM in solution rather than cutting down the HPAM chain, and this action is reasonably related to the amid group of HPAM.



# Sulfide influence on HPAM viscosity and the concerning mechanism



## INTRODUCTION

Engineering Research Center of Microbial Enhanced Oil Recovery of the Ministry of Education was established in Oct. 2013, and was built based on East China University of Science and Technology. The center consists of four platforms as key Technology Development & Integration, Engineering R&D, Scaling up & Pilot Protocols, and Technology Transfer.

## VISION

As one of the leading research center, it strives to attract nurture frontiers in green and sustainable technologies in microbial enhanced oil recovery, and to serve as an open platform for research, technical training, technology transfer, information sharing, and international collaboration.

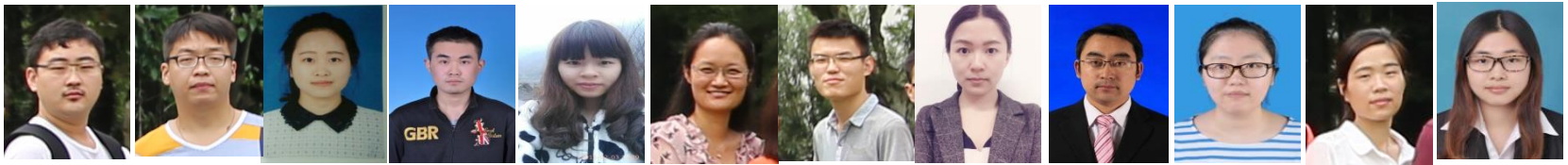
## MISSION

The objectives of the center are focus on cost-effective approaches for enhancement of energy recovery. The on-going tasks include (1) roles of microbial community in-situ petroleum, (2) bio-conversion of residues oils into natural gas in oil reservoirs, (3) microbial and bio-based surfactants, and (4) biofixation and bio-conversion of carbon dioxide to methane energy by geo-microorganisms in-situ oil reservoirs.



# Sulfide influence on HPAM viscosity and the concerning mechanism

## Faculty and students in our group



## Biodegradation & Products



## Microbial communities



## Academic members (including Postdoctors)

# **Thanks for your attentions**

**East China University of Science and Technology**

**21<sup>th</sup> July, 2016**