Narrative Progress Report

PRF#57095-DNI7

Project Title: Study of New Polybetaine's Self-Assembly and Their Effect on Paraffin Inhibition

PI: Nurxat Nuraje, Texas Tech University

Overview:

The proposed work focuses on synthesizing Polybetaines with different hydrocarbon groups and studying both their assembly in different solvents and their inhibition mechanism of paraffin crystallization. The specific objectives are (1) to synthesize Polybetaines with different alkyl lengths(HMPBs) and to characterize them using NMR, FTIR, and GPC; (2) to study their assembly properties in different conditions including different pHs, solvents with different polarity, ionic strengths, and temperatures using cryo-TEM, DLS, and viscometer; (3) to understand the effect of hydrophobically-modified polybetaines on the nucleation and crystal growth of paraffin through characterizations using microscopy techniques. The proposed work is anticipated to establish a new class of polybetainic paraffin inhibitors, a new understanding on the inhibition of paraffin crystallization and guidelines for designing paraffin inhibitors for crude oils.

Tasks of project (from 07/01/2016—08/31/2018):

Task 1 (2016- 2017): We will synthesize novel monomers and HMPBs (from C8 to C18). The composition and Molecular weights of synthesized monomers and polymers will be further confirmed by NMR, FTIR, and GPC. In parallel with the above random radical polymerization (RRP) synthesis, Reversible addition-fragmentation chain transfer (RAFT) will be developed to synthesize these HMPBs with controlled molecular weight. The NMR and GPC techniques will be used for characterization of these polymers and their polydispersity.

Task 2 (2016- 2017): Self-assembly of Polybetaines: Hydrodynamic, conformational, molecular, and thermal properties of monomers and HMPBs (C8-C18) will be investigated by DLS, zetasizer, cryo-TEM, GPC.

Task 3 (2017- 2018): The Paraffin inhibition mechanism of the HMPBs: The physical-chemical and rheological characteristics of model oil and oil mixtures in particular, the dynamic and kinematic viscosity, paraffin content, paraffin crystal structure, - will be studied. This work was extended to August 31 of 2018 at no cost.

For rheological studies, model waxy oil samples are prepared from paraffin waxes in decane, and straight chain alkanes of carbon numbers (C*n*) n = 24, 28, 32, and 36 as paraffin waxes will be examined.

Pour points will be measured according to ASTM D97 and ASTM

Wax crystal morphologies will be determined with a polarized microscope.

Wax deposition inhibition: Inhibition of wax deposition was tested on a "Cold Finger" test.

Results of Second Half- Year (from 09/01/ 2017- 08/31/2018):

According to our tasks, we have finished task 1 to some part of task 3. The hydrophobically modified polybetianes (P8, P12, P14, and P16) with different haydrocarbon tails were successfully synthesized. The molecular weight and PDI for P12 were found to be 70,080 g/mol and 1.2 respectively. Their self-assembly behaviors were investigated from low pH to high pH with zeta potential change. As shown in Figure 1, the isoelectric point for P12 was between pH 1 and 2. The self-assembly structures were changed from spherical, cylindrical to fractal structures as shown in Figure 1. At the same time, we have accomplished paraffin deposition experiments for these polybetaines via cold finger tests.

In the cold finger experiment, a model wax solution including either Hexatriacontane ($C_{36}H_{74}$, the purity of 98%) or Tetracosane ($C_{24}H_{50}$, the purity of 99%) was prepared in decane solvent. The solution was kept at 50º Celsius and further added with calculated polybetaines. The concentration of added hydrphobically modified polybetaines was varied from 100ppm to 500 ppm. Next a thin gold glass tube was inserted inside the above solution to provide cold surface for deposition of waxes and kept for at least four hours. The cold temperatures applied was either 0 ºCelsius or -17º Celsius. Later, the deposited paraffin on the cold surface of the thin cold tube was collected and weighted to evaluate the paraffin inhibition performance of the synthesized polybetaines.

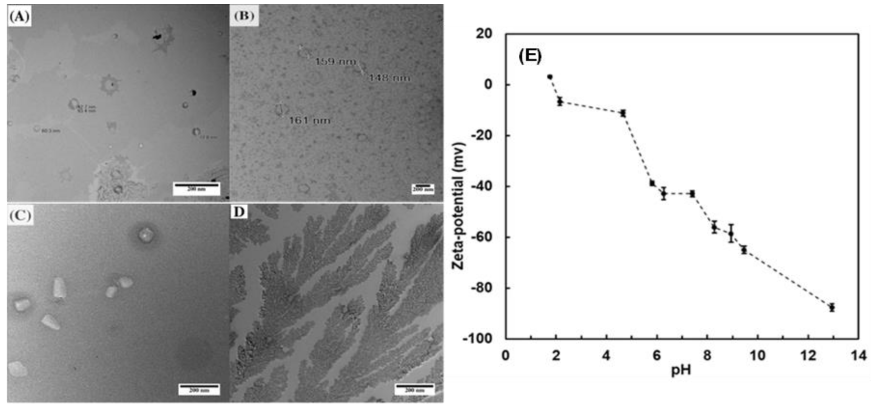

Figure 1. TEM images of the Poly (dodecylaminocrotonate methacrylic acid) formed in the aqueous dispersions at different pH values. Slight contrast change was made in TEM images (A) pH 1.0, (B) pH 3.0, and (C) pH 10.0, (D) pH 12.0. The solution concentration is 10mg/ml. (E) zeta potential change of Poly (dodecylaminocrotonate methacrylic acid) vs. pH.

As shown in Figure 2 A, the longer the hydrocarbon chain in the polybetaines, the better the paraffin inhibition performance. It can be learned from the figure 2 that C16 hydrocarbon grafted polybetaines (P16) is the best paraffin inhibitor among the four polybetaines. At the same time, Figure 2 (B) shows that P8 hydrocarbon grafted polybetaines show the best paraffin inhibition performance at the 500ppm.

Impact of the research and next generation educational training: with support of the project, we successfully synthesized hydrophobically modified polycarboxybetaines for the first time. The PDI of the polybetaines was controlled to be 1.2 and their molecular weight was around 70080g/mol. The synthesized polybetaines showed interesting self-assembly behaviors from spherical micelle to cylindrical and fractral assembled structures. These assembly structures are very important to understand the fundamental of the polybetaines. Their excellent paraffin inhibition performance indicated that the polybetaines can be applied to oil-field industry as paraffin inhibtor. Through the project, PI has successfully established polybetaines program in his early career and trained graduate students to be expert in this field. A graduate student wrote a Master thesis titled "*Synthesis and Self-assembly of Hydrophobically Modified Polybetaine (HMPB)*". Two papers were published in peer review journals and one manuscript submitted to *Macromolecules* is under review process. With partial support of this project, several papers were published in peer review journals. Six Undergraduate students were engaged in this project under course number (ChE4000). The PI also included the research results in his newly developed courses which are Chemical Engineering Applications in Energy Science (ChE4391/5391) and colloid science and engineering course (ChE4393/5393).

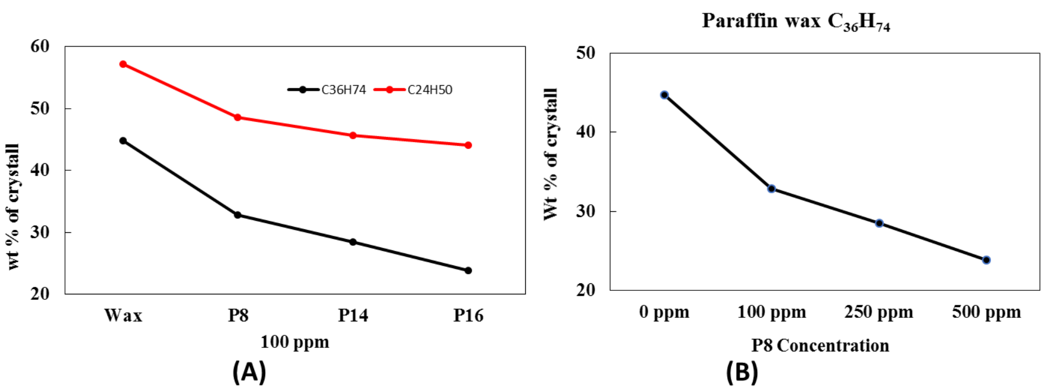

Figure 2. (A) wax ($C_{36}H_{74}$ and $C_{24}H_{50}$) deposition efficiency for P8, P14, P16 and no polybetaines at 100ppm concentration. (B) Wax ($C_{36}H_{74}$)deposition efficiency for P8 at concentrations of 100, 250 and 500 ppm