

# Giant surfactants-stabilized N<sub>2</sub>-foam to enhance oil recovery after waterflooding

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## 1. Experimental section

### 1.1 Materials

VPOSS (Octavinyl POSS) and 4-(dimethylamino) pyridine, with purity of 95.0 and 99.0 individually, were supplied by Aikon (China). The purity of *p*-toluenesulfonic acid (TsOH) from HWRK Chem (China) is 98.0%. 2-hydroxyethyl 2-bromoisobutyrate was purchased from J&K (China) with purity of 95.0%. Methyl alcohol (99.5%), trifluoromethanesulfonic acid (98.0%), styrene (99.0%) and 4-formylbenzoic acid (98.0%) were supplied by Macklin (China). N,N'-diisopropylcarbodiimide (DIPC, 98.0%), cuprous bromide (CuBr, 99.0%), triethylamine (Et<sub>3</sub>N, 99.0%), (boc-aminooxy) acetic acid (>98.0%), and N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99.0%) were purchased from Aladdin (China). Dichloromethane, acetone, dioxane, toluene (with purity ≥99.5% for all of them), sodium carbonate, sodium chloride (with purity ≥99.8% for both), magnesium sulfate (≥99.0%) and hydrogen chloride (36.0-38.0%) were obtained from Sinopharm chemical reagent (China).

### 1.2 Characterization

Referenced by the HLB value of potassium oleate-span 80 hybrid, the HLB values of APOSS-PS<sub>50</sub> and HPAM, with the mixture of isopropyl alcohol and toluene (m<sub>IA</sub>: m<sub>T</sub> = 100: 15) as solvent, were determined by cloud point methodology. A certain amount of potassium-oleate hybrid (total concentration 2.0 wt%, Table S1) was dissolved in 25 mL solvent, then the transparent solution was added with water until it changes to be misty (3#font looks misty through solution), and the water

volume was recorded. Furthermore, the standard curve of HLB value versus water volume was obtained for potassium oleate-span 80 system. Herein, the HLB value of HPAM and APOSS-PS<sub>50</sub> were determined according to the potassium oleate-span 80 standard curve and water volume.

The experimental process of concentration screening is shown as follows: Firstly, the foaming volume  $V$  was used as the evaluation index to screen the concentration of foaming agent AOS. Then, under the optimal concentration of AOS, the concentration of foam stabilizers (HPAM and APOSS-PS<sub>50</sub>) was determined with foam stability index (FSI) as the evaluation parameter. To be specific, during the test, 50 mL foaming solution was placed in a 1000 mL measuring cylinder, then N<sub>2</sub> gas was filled into it at flow rate of 0.5 mL·min<sup>-1</sup> to produce foam. The maximum foam volume  $V_{\max}$  and its half-life  $t_{1/2, \text{FV}}$  were recorded, and FSI was calculated accordingly. FSI calculation method and formula are shown in Fig S1 and equation (S2-1).

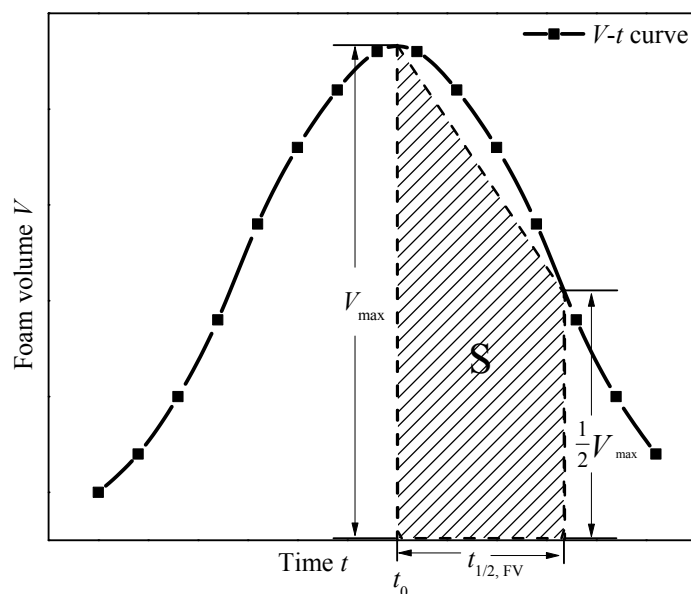


Figure S1. Schematic of FSI calculation

$$\text{FSI} = S = \int_{t_0}^{t_0+t_{1/2, \text{FV}}} f(t) dt \approx \frac{3}{4} V_{\max} t_{1/2, \text{FV}} \quad (\text{S2-1})$$

Where  $V=f(t)$ .

### 1.3 Synthetic Procedures

#### (1) VPOSS-OH

Trifluoromethanesulfonic acid (45 mg) and VPOSS (188 mg) were dissolved in

25 mL CH<sub>2</sub>Cl<sub>2</sub>, stirred for 3 h, followed by dilution with CH<sub>2</sub>Cl<sub>2</sub>. Afterwards, the solution was added into carbonate solution and solid magnesium sulfate successively for lavation and desiccation, then evaporated to produce intermediate product VPOSS-OTf. The intermediate was hydrolyzed in dioxane-sodium carbonate aqueous solution for 6 h. After removal of solvent, the white powder product VPOSS-OH was obtained.

(2) *VPOSS-CHO*

An amount of VPOSS-OH (651 mg), 4-formylbenzoic acid (158 mg), 4-(dimethylamino) pyridine (122 mg) and TsOH (173 mg) were dissolved in 30 mL CH<sub>2</sub>Cl<sub>2</sub>, subsequently cooled to 0°C and stirred for 10 min. Then, DIPC (189 mg) was added dropwise into the solution via a syringe. The mixture was warmed up to 25°C and stirred for 12 h. After filtration, lavation, desiccation and solvent removal of the mixture, the white solid VPOSS-CHO was prepared.

(3) *BocNH-O-Br*

2-hydroxyethyl 2-bromoisobutyrate (211 mg), (boc-aminooxy) acetic acid (201 mg), 4-(dimethylamino) pyridine (122 mg) and TsOH (173 mg) were mixed in 30 mL CH<sub>2</sub>Cl<sub>2</sub>, stirred for 10 min at 0°C. After DIPC (189 mg, 1.5 mmol) was added dropwise via a syringe, the mixture was stirred for 12 h at 25°C. The product BocNH-O-Br was obtained via filtration, lavation, desiccation and solvent removal of the mixture.

(4) *BocNH-O-PS<sub>50</sub>*

The polymerization was conducted by mixing a certain amount of BocNH-O-Br (260 mg), styrene (25 g), CuBr (100 mg), PMDETA (200 mg) and toluene (14 mL) under nitrogen atmosphere, transported into 110°C oil bath for 200 min, immersed in liquid nitrogen, and then precipitated three times by cold methanol to produce the product BocNH-O-PS<sub>50</sub>.

(4) *NH<sub>2</sub>-O-PS<sub>50</sub>*

BocNH-O-PS<sub>50</sub> was dissolved in 10 mL hydrogen chloride solution, stirred for 4 h, followed by addition of Et<sub>3</sub>N to adjust pH. After solvent removal, the solid NH<sub>2</sub>-O-

PS<sub>50</sub> was obtained.

## 2. Results and discussion

### 2.1 HLB value determination

The results of HLB value determination experiments are shown in Table S1 and Fig S1.

Table S1 HLB value versus water volume

Number	m <sub>PO</sub> : m <sub>span</sub>	HLB	Water volume /(mL)
1	100: 0	20.0	3.20
2	95: 5	19.2	2.56
3	90: 10	18.4	2.10
4	85: 15	17.6	1.80
5	80: 20	16.9	1.60
6	70: 30	15.3	1.25
7	60: 40	13.7	1.00
8	50: 50	12.1	0.74
9	40: 60	10.6	0.62
10	30: 70	9.0	0.53
11	20: 80	7.4	0.45
12	10: 90	5.9	0.40
13	0: 100	4.3	0.33

m<sub>PO</sub>: mass of potassium oleate; m<sub>span</sub>: mass of span 80.

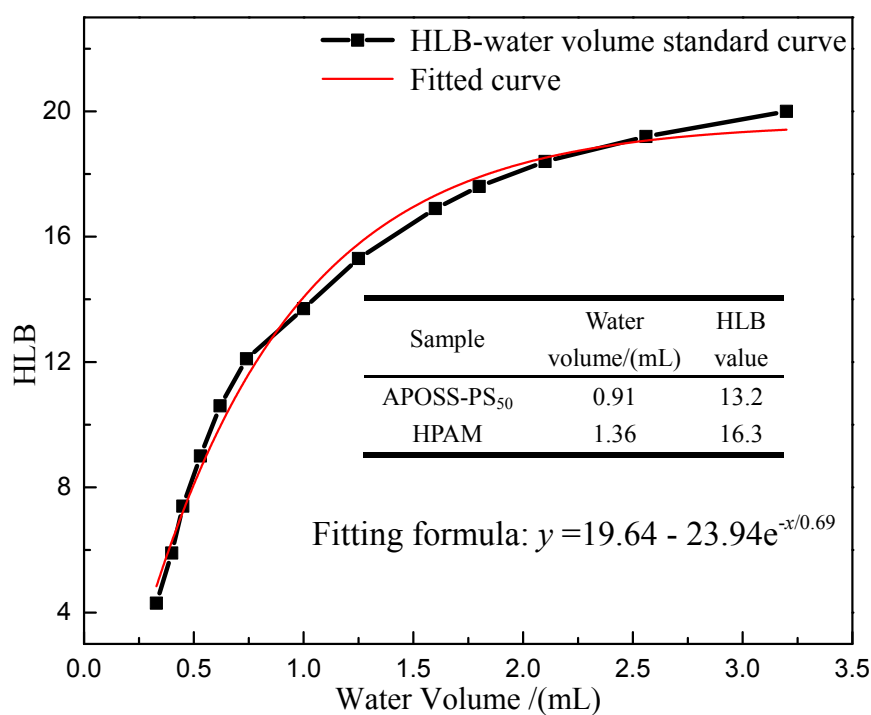


Figure S2. HLB value versus water volume standard curve

The water volume at cloud point for APOSS-PS<sub>50</sub> and HPAM solution were 0.91 mL and 1.36 mL correspondingly, and their HLB values were 13.2 and 16.3 according to the fitting formula (Table S1 and Fig S2).

## 2.2 foaming agent and foam stabilizers concentration screening results

As an overall evaluation parameter of foam property, FSI value can quantitatively reflect foamability and foam stability by calculating the integral of  $V-t$  curve from  $t_0$  to  $t_0+t_{1/2, FV}$ [1,2]. Therefore, in our work, FSI value as employed to optimize foaming solution concentration ratio. The results are shown in Fig S3.

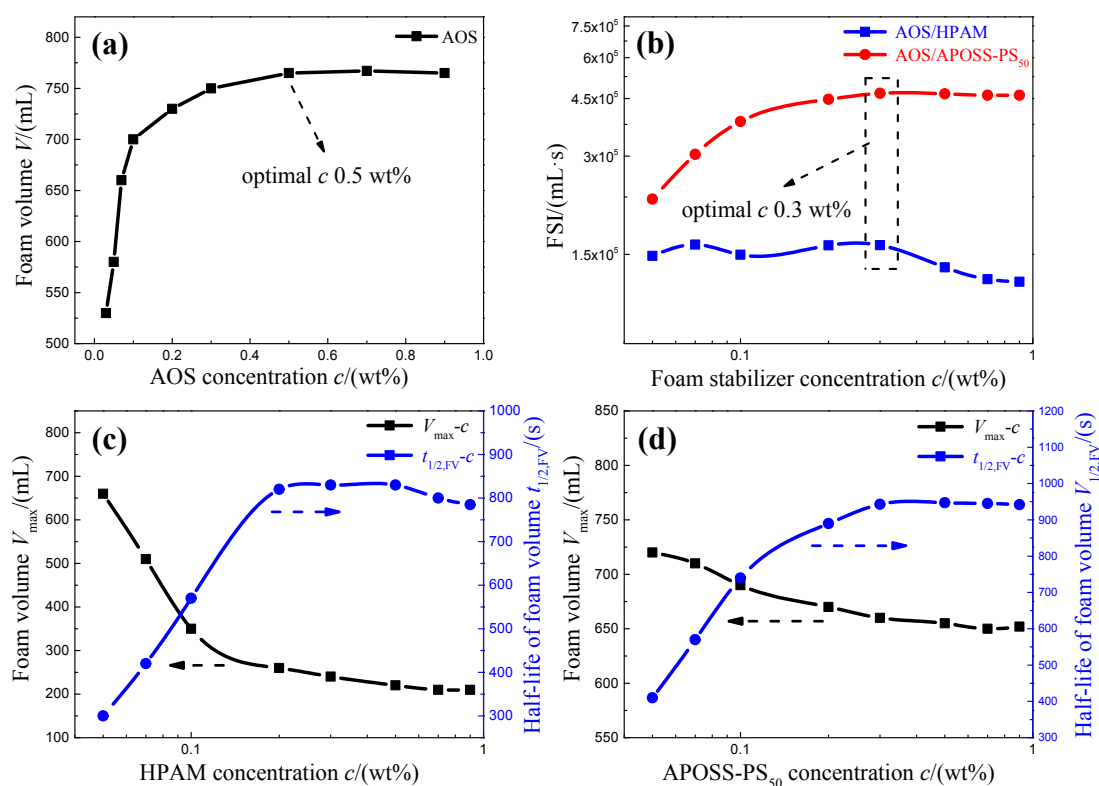


Figure S3. Foam solution concentration optimization

(a) Foam volume vs AOS concentration, (b) FSI value vs foam stabilizer concentration, (c)、(d) Foam volume and half-life vs HPAM and APOSS-PS<sub>50</sub> concentration respectively

According to Fig S3 (a), in the absence of foam stabilizer, foam volume first increased and then tended to remain unchanged with the increase of AOS concentration. The maximum foam volume was 765 mL with the minimum AOS concentration 0.5 wt% as the optimum foaming agent concentration for subsequent tests. In Fig S3 (b), with the fixed AOS concentration, FSI value of foam system showed a small decline trend with the increase of HPAM concentration. The

maximum FSI value was 159900 mL·s corresponding to HPAM concentration 0.3 wt%. Meanwhile, with the rise of APOSS-PS<sub>50</sub> concentration, FSI value first increases and then tends to be unchanged. The maximum FSI value is 466785 mL·s with APOSS-PS<sub>50</sub> concentration 0.3 wt%. The reasons for the above experimental phenomena are as follows: 1) Although HPAM can effectively enhance foam stability, it will significantly damage foamability. As HPAM concentration increases,  $t_{1/2, FV}$  enlarged with much decreased  $V_{max}$  (Fig. S3 (c)), leading to a low FSI value. 2) APOSS-PS<sub>50</sub> can markedly strengthen foamability and foam stability simultaneously. With the increase of APOSS-PS<sub>50</sub> concentration,  $t_{1/2, FV}$  increases obviously as well as slightly declined  $V_{max}$  (Fig. S3 (d)), resulting in much high FSI value. Consequently, according to FSI values, 0.3 wt% was selected as optimal foam stabilizer concentration for HPAM and APOSS-PS<sub>50</sub>.

### 2.3 $\chi$ value determination

The  $\chi$  (effective interaction parameter) value can be calculated as follows:

$$\chi = \alpha T^{-1} + \beta \quad (\text{S2-2})$$

Where  $\alpha$  and  $\beta$  are system dependent coefficients. Assuming that the  $\chi$  has an identical relationship with temperature for POSS-based giant surfactants and that the scaling relationship of  $\chi \sim T^{-1}$  still holds, we can roughly estimate the value of  $\chi$  at ODT to be 0.25 using the reference volume ( $v_0$ ) of 118 Å<sup>3</sup> (which corresponds to an  $N$  of 59) [3-6]. Besides,  $f_{PS}$  (PS segment volume fraction) of APOSS-PS<sub>50</sub> was 0.85, calculated from molecular mass and density data. Thus,  $f_{APOSS} = 1 - f_{PS} = 0.15$ , and  $N = N_{PS}/f_{PS} = 59$ .

### 2.4 Determination of liquid fraction in foam

LF (Liquid fraction in foam), the ratio of liquid volume in foam to foaming solution volume, is calculated as follows:

$$LF = \frac{V_f}{V_{fs}} = \frac{V_{fs} - V_{rfs}}{V_{fs}} \quad (\text{S2-3})$$

Where  $V_f$ ,  $V_{fs}$  and  $V_{rfs}$  are liquid volume in foam, foaming solution and residual solution after foaming process, respectively.

## 2.5 Gas-liquid ratio and gas friction screening results

At the optimal concentrations (AOS 0.5 wt%, APOSS-PS<sub>50</sub> 0.3 wt%, HPAM 0.3 wt%), the displacement differential pressure  $\Delta P$  was used as evaluation index to screen the injection gas-liquid ratio. The results are shown in Fig S4.

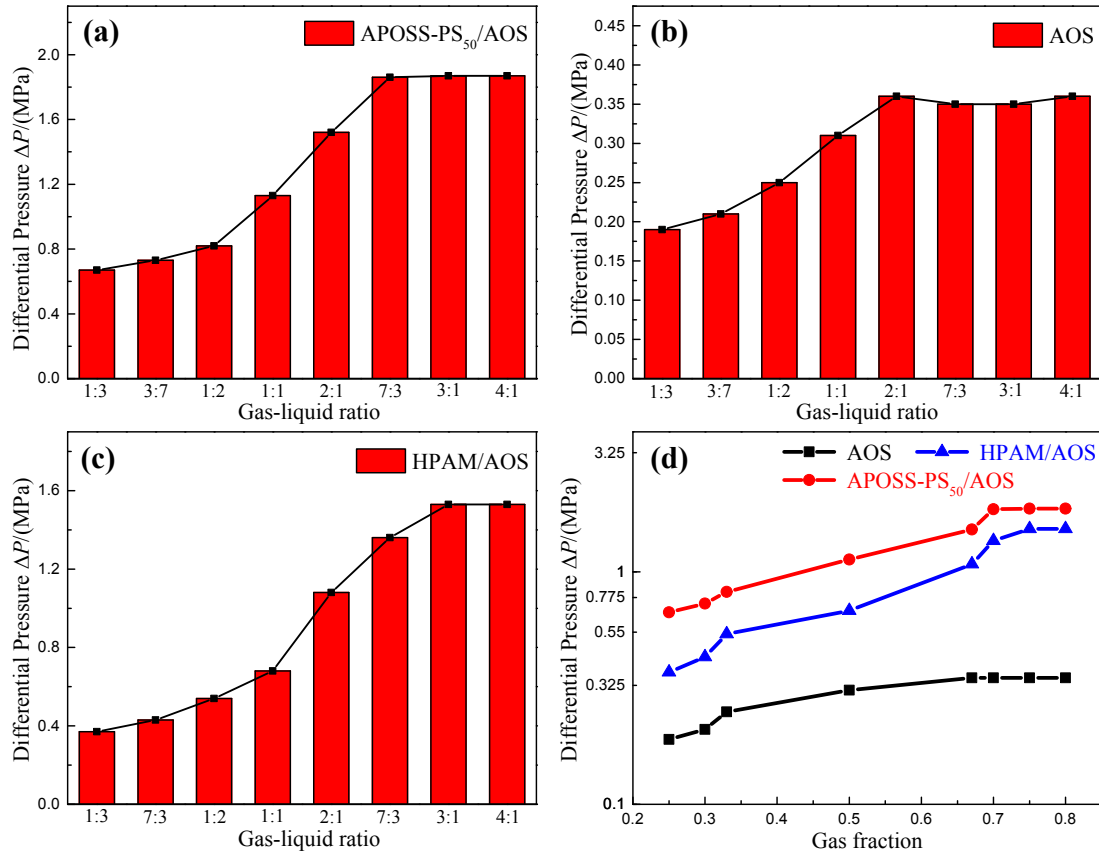


Figure S4. Injection gas-liquid ratio screening experiment

(a)~(c)  $\Delta P$  vs gas-liquid ratio and (d)  $\Delta P$  vs gas friction in AOS, HPAM/AOS and APOSS-PS<sub>50</sub>/AOS foam flowing experiments

According to Fig. S4, with the increase of gas fraction or gas-liquid ratio,  $\Delta P$  of all foam showed a trend—first increasing and then unchanged. Herein, the minimum gas-liquid ratios corresponding to the maximum  $\Delta P$  were 7:3, 3:1 and 2:1 (converted into gas fraction of 0.7, 0.75 and 0.67 respectively) corresponding to APOSS-PS<sub>50</sub>/AOS, HPAM/AOS and AOS. Therefore, the gas-liquid ratio 3:1 (gas fraction 0.75) corresponding to the maximum  $\Delta P$  in all foam flowing experiments was assured as the optimum.

## 2.6 Apparent viscosity $\eta$ determination

Apparent viscosity  $\eta$  calculation formula is shown as follows[7]:

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{\tau \times K_{\sigma}}{\Omega \times K_{\gamma}} \quad (\text{S2-4})$$

Where  $\eta$  (mPa·s) is apparent viscosity,  $\sigma$  (Pa) is shear stress,  $\dot{\gamma}$  (s<sup>-1</sup>) is shear rate,  $\tau$  ( $\mu\text{N}\cdot\text{m}$ ) is torque,  $\Omega$  (rad·s<sup>-1</sup>) is angular rate. Besides,  $K_{\sigma}$  and  $K_{\gamma}$  are stress factor and strain factor, respectively. Meanwhile,  $\sigma = K_{\sigma} \times \tau$ ;  $\dot{\gamma} = K_{\gamma} \times \Omega$ .

### 2.6 Comparative molecular size analysis of APOSS-PS<sub>50</sub>, AOS and HPAM

We determined the molecular weight of APOSS-PS<sub>50</sub> by MALDI TOF mass spectrometry, then made a comparative analysis on molecular weight and molecular size AOS, APOSS-PS<sub>50</sub> and HPAM. The results were added into SI 2.6, as shown in Fig S5 and table S2.

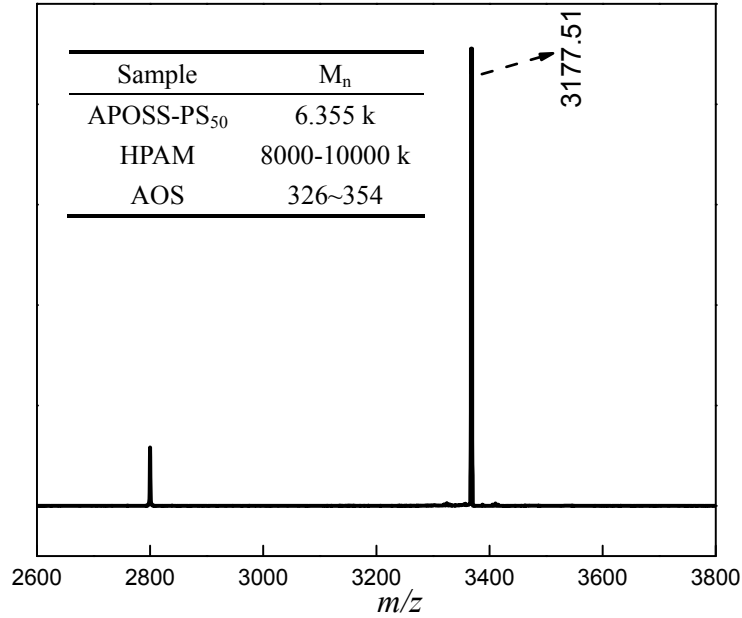


Figure S5. MALDI-TOF mass spectra of APOSS-PS<sub>50</sub>, the inset table shows M<sub>n</sub> of samples

From Fig S5 and its inset Table, the molecular weight and molecular size of APOSS-PS<sub>50</sub>, HPAM and AOS are significantly different, and their order of molecular size is HPAM >> APOSS-PS<sub>50</sub> >> AOS. The differences in molecular sizes will lead to significant changes for the foam properties: 1) As for AOS, the small molecular weight and size limit its viscosifying performance [7,8]. 2) For APOSS-PS<sub>50</sub>, due to the smaller molecular weight and relatively higher hydrophobicity with comparison to HPAM, APOSS-PS<sub>50</sub> molecule is easy to migrate in its aqueous solution with a high rate, bring about more molecules diffusion into fluid layer



adjacent to foam surface and improved viscoelasticity of foam film [9,10]. 3) Compared with HPAM, the smaller molecular weight of APOSS-PS<sub>50</sub> is also helpful to weaken its adsorption for AOS molecules, thus reducing the damage to foamability from foam stabilizer.

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