

An innovative approach to asphaltene formation damage prevention

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The aim of this work is to present an innovative approach to prevent formation damage induced by asphaltene deposition. Our approach consists in the treatment of the formation rock by means of diblock copolymers apt to be adsorbed onto rock. In this way, the rock sites already occupied by such molecules, the asphaltene deposition is drastically reduced.

Diblock copolymers are self-assembling systems, which adopt a segregated structure in a selective solvent, the insoluble block form a core and the soluble block form brushes. We used the copolymer polystyrene-polyvinyl-2-pyridine, PS-PV2P, toluene is a good for the block PS and poor for the block PV2P.

The structure of the interface can be described as a thin layer of dense PVP and a brush of extended PS chains. From a toluene solution, the copolymer adsorbs onto rock through the PV2P block, the polystyrene tail extending toward the solution (Fig. 1).



Fig. 1. PS-PV2P: (a) diblock, (b) micelle, (c) adsorption.

The effect of PS to PV2P ratio and concentration were studied for different oil rates. Experiments were performed in a Hassler cell, using sandstone cores ($\phi \sim 10\%$, $30 < K < 500 \text{ mD}$), the copolymer solution was injected then the oil (Table 1). Samples of PS-PV2P, of two different sequence ratio, were provided by Charles Sadron Institute: 552 and 569 (Table 2).

Table 1. Weyburn and Hassi Messaoud (HM) oil properties.

Oil	$\rho, \text{g/ml}$	μ, cP	S(%)	A(%)	R(%)	A(%)
HM	0.84	0.98	70.5	25.5	3.3	0.15
Weyburn	0.87	0.91	40.1	46.1	8.5	5.3

Table 2. Properties of copolymers used. R is the radii of occupied surface and R_{PS} is the PS ratio in toluene [1].

PSx-PV2Py	MW	R, nm	R_{PS} , (nm)	x/y	CMC (ppm)
552	113090	4.4	5.69	2.48	13.125
569	184400	3.6	4.05	8.93	21.402

The effect of prevention of asphaltene-induced damage was observed. Figure 2 compares ΔP through the core when PS-PV2P is injected or not. The permeability reduction ($R_m = K_o/K$) is improved in 20% when the PS-PV2P is injected. Besides, monomers and micelles of the copolymers PS-PV2P irreversibly adsorb onto silica surfaces [2].

We studied the influence of x/y and observed that copolymer 569 is more efficient preventing asphaltene deposition (Fig. 3). In presence of 569, the damage is inhibited ($R_m \sim 1$). It might be explained by the surface coverage due to the characteristics of PS-PV2P-569.

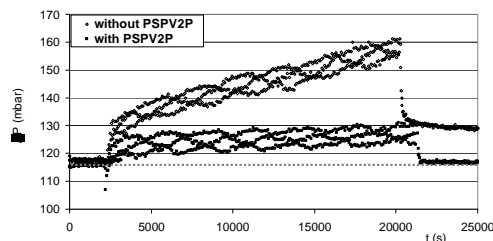


Fig. 2. Inhibition effect of copolymer PS-PV2P 552.

According Table 2, the surface occupied (R_{PS}) by an adsorbed chain 552 is bigger. Besides, the bigger the x/y ratio the lower the distance D [3]. Figure 4 shows schematically, the distance between adsorbed polymers for both sequences, D is smaller for PS-PV2P-569: $D_{552} > D_{569}$ and copolymer 569 should give a better surface coverage. Therefore the screen formed by PS-PV2P-569 is denser and gives a steric protection to the surface. On the other hand, as $y_{569} \gg y_{552}$, copolymer 569 possesses a stronger affinity to surface and a higher rate of adsorption than 552.

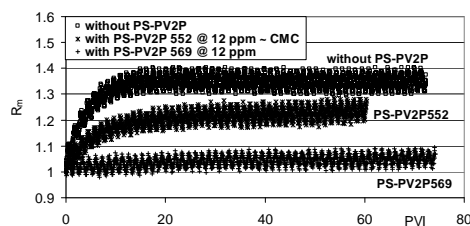


Fig. 3. Effect of PS/PV2P ratio, Weyburn crude oil, 30ml/h.

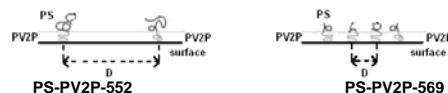


Fig. 4. Scheme of distance between adsorption sites, D.

Finally, the effect of concentration of copolymer 569 was studied. For solutions of 569 below CMC, the prevention of asphaltene deposition is more efficient compared to solutions above CMC. Below CMC the surface occupied by monomers is much smaller than above CMC [2]. In consequence, the surface coverage is more uniform and the screen is denser, then inhibition of asphaltene deposition is more important.

In conclusion, the diblock copolymer tested is an efficient way to diminish asphaltene induced formation damage.

References

- [1] Higo, Y., et al. (1983) *Polymer Journal* 15, 367-375.
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- [3] Huguenard, C., Pefferkorn, E. (1994) *Macromolecules* 27, 5271-5276.