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► **To cite this version:**

G. Muller, J. Huguet, L. Merle, M. Grisel, L. Picton, et al.. Associative Polymers and Physical Gels Derived from Natural Biopolymers. *Revue de l'Institut Français du Pétrole*, EDP Sciences, 1997, 52 (2), pp.232-234. 10.2516/ogst:1997025 . hal-01866928

HAL Id: hal-01866928

<https://hal-normandie-univ.archives-ouvertes.fr/hal-01866928>

Submitted on 25 Mar 2019

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ASSOCIATIVE POLYMERS AND PHYSICAL GELS DERIVED FROM NATURAL BIOPOLYMERS

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Various natural, synthetic and semi-synthetic hydro-soluble polymers are largely used in oil-field operations where the control of rheology of aqueous phases is of primary importance. In water-based drilling muds they serve a number of functions and they are added mainly i. to impart desirable rheological properties to the fluid and ii. to affect solid particle interactions.

Such objectives are realized by using polymers systems showing shear-thinning and thixotropic properties with high viscosity at low shear and low viscosity under the high shear conditions around the drill bit. Moreover such systems should display thermal, mechanical and chemical stability.

Two types of hydrophilic polymers are largely used for developing high solution viscosity: high molecular weight flexible acrylic and acrylamide polymers and rigid xanthan exopolysaccharide. With such systems the viscosity enhancement relies on extension and physical entanglements of long solvated chains. The main disadvantage is that irreversible breakage of polymer backbone could result from high shear rates conditions.

Polymer systems showing high viscosity as a consequence of large "apparent molecular weight" because of the establishment of intermolecular interactions of low energy present many advantages as candidates for drilling muds. They can be derived from precursors of medium molecular weight. Moreover only intermolecular interactions are affected at high shear rate. Associating polymers, i.e. polymers the hydrophilic main chains of which have been properly modified by introducing hydrophobic groups and weak physical gels are good examples of such systems.

The different systems we have chosen to study in dilute and semi-dilute concentration regimes are derived from natural biopolymers.

They differ essentially by the nature of the hydrophilic main chain: ionicity, length, flexibility and by the type of

modification: alkyl and fluoroalkyl hydrophobic modifiers, non covalent ionic interactions.

They are:

- Alkyl derivatives issued from neutral (HEC) and ionic (CMC) cellulosic ether derivatives ;
- Alkyl and fluoroalkyl derivatives from neutral (Pull) and ionic (CMP) bacterial polysaccharide pullulane ;
- Weak physical gels resulting from complex formation between borate ions and the neutral fungal polysaccharide schizophyllan. The phase diagram of such a system is given by the Figure 1 as a function of polymer and borax concentration (25°C, 0.5 M NaCl).

Concerning the hydrophobically modified water soluble polymers, we report different experimental data proving that

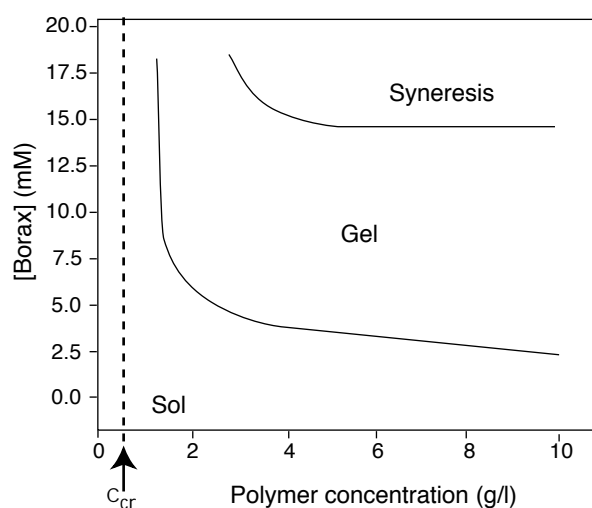


Figure 1

Phase diagram fro schizophyllan-borax mixtures at 25°C
(0.5 M NaCl)

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the overall solution properties (below and above the critical overlap concentration) depend on many factors governing the hydrophobic/hydrophilic balance. These factors are related to:

- The nature of parent polymers, as shown in Table 1, where are reported the modified/precursor viscosity ratio for different associative system ($C_p = 3 \text{ g/l}$, 0.1 M NaCl).

TABLE I

Viscometric behaviour of different associative polysaccharides

Polysaccharides	CMC	HEC	CMP	CMP
neutral/charged	charged	neutral	charged	charged
precursor Mw (g/mol)	300 000	500 000	210 000	320 000
type of hydrophobe	alkyl C_{16}	alkyl C_{16}	alkyl C_{16}	fluoroalkyl $C_2H_4-C_8F_{17}$
hydrophobe content	6%	0.6%	4.5%	4.5%
$\eta_{red. \text{ modified}}/\eta_{red. \text{ precursor}}$ ($C_p = 3 \text{ g/l}$)	1.5	2.4	3.1	0.85

- The type of hydrophobic modification and/or crosslinker including the extent of modification, the nature and the length of hydrophobic modifiers, their distributions. As an example, the viscometric behaviour of the modified CMC has been studied as a function of the extent of modification and polymer concentration (Fig. 2).

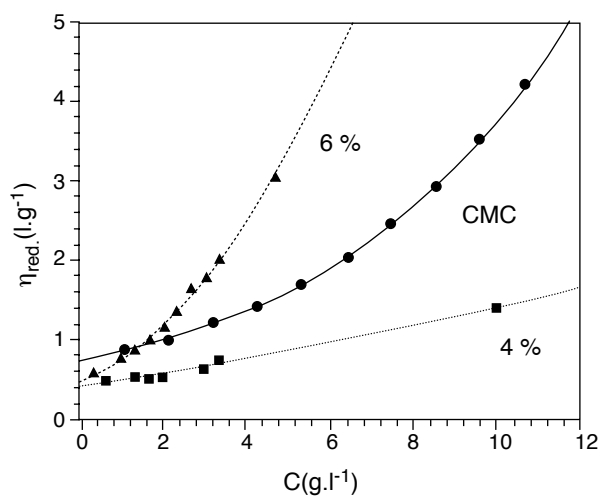


Figure 2

Effect of C_{16} content on viscometric properties of modified CMC (0.1 M NaCl)

- The environmental conditions (shear rate, temperature, salinity, cosolvent, etc.). The salt dependence of a neutral associative HEC ($C_p = 20 \text{ g/l}$) is shown on Figure 3.

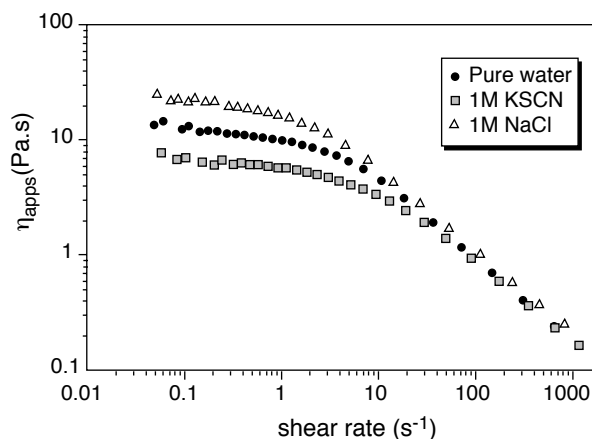


Figure 3

Flow curves of HMHEC ($C_p = 20 \text{ g/l}$) in pure water, 1 M NaCl and 1 M KSCN (25°C)

Lytotropic salt (NaCl) reinforces intermolecular hydrophobic associations while the chaotropic salt (KSCN) induces a disruption of such associations. Hydrophobic interactions seem to be mainly related to the water structure.

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Final manuscript received in January 1997