

ASSOCIATIVE POLYMERS AND PHYSICAL GELS DERIVED FROM NATURAL BIOPOLYMERS

G. MULLER, J. HUGUET, L. MERLE, M. GRISEL, L. PICTON, I. BATAILLE, D. CHARPENTIER and K. GLINEL

CNRS¹

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

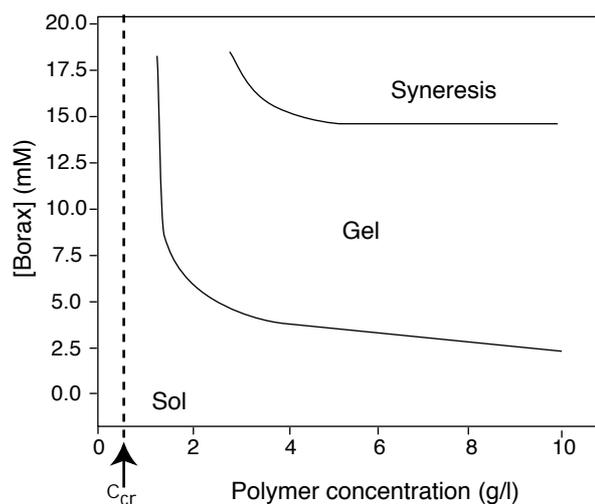


Figure 1

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

(1) Polymères, Biopolymères et Membranes, Université de Rouen, 76821 Mont-Saint-Aignan Cedex - France

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).

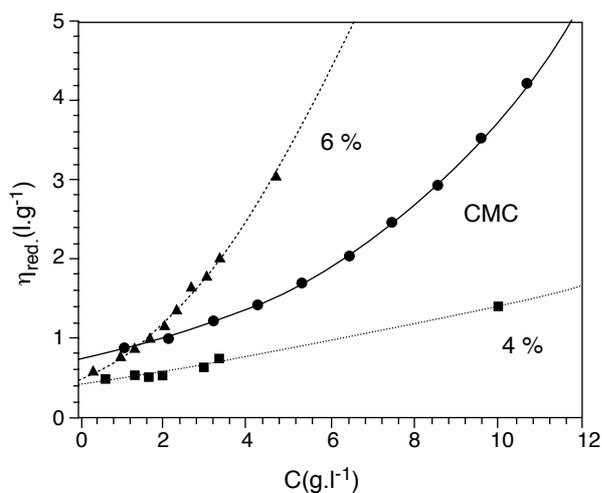


Figure 2

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.

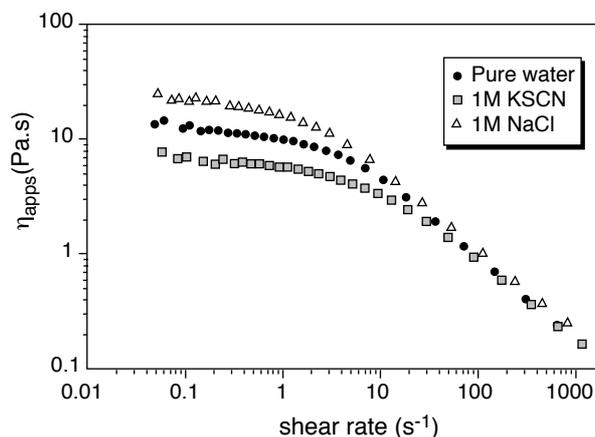


Figure 3

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.

REFERENCES

- Capron I., M. Grisel and G. Muller (1995), On-line size exclusion chromatography and multi-angle laser light scattering of high molecular weight polysaccharides. *International Journal of Polymer Analysis and Characterization*, **2**, 9.
- Grisel M. and G. Muller (1996), Rheological properties of schizophyllan in presence of borate ions. *Progress in Colloids and Polymer Science*, in press.
- Grisel M. and G. Muller (1996), The salt effect on the physical interactions occurring for schizophyllan in the presence of borate ions. *Macromolecular Chemistry and Physics*, in press.
- Picton L., L. Merle and G. Muller (1995), Solution behaviour of hydrophobically associating cellulosic derivatives. *International Journal of Polymer Analysis and Characterization*, **2**, 103.
- Picton L., G. Mocanu, D. Mihaï, A. Carpov and G. Muller (1995), Chemically modified exopolysaccharide pullulans: physico-chemical characteristic of ionic derivatives. *Carbohydrate Polymers*, **28**, 131.
- Picton L. and G. Muller (1996), Rheological properties of modified cellulosic polymers in semi-dilute regime: effect of salinity and temperature. *Progress in Colloids and Polymer Science*, in press.

Picton L. and G. Muller (1996), Solvent-polymer interaction in associative polymers/aqueous media systems. *Macromolecular Chemistry and Physics*, in press.

Mocanu G., A. Carpov, S. Chapelle, L. Merle and G. Muller (1995), Chemically modified II. New hydrophobically substituted derivatives. *Can. J. Chem.*, **73**, 1933.

Charpentier D., G. Mocanu, A. Carpov, S. Chapelle, L. Merle and G. Muller (1996), New hydrophobically modified carboxymethylcellulose derivatives. *Carbohydrate Polymers*, in press.

Bataille I., J. Huguet, G. Muller, G. Mocanu and A. Carpov (1996), Associative behavior of hydrophobically modified carboxymethylpullulan derivatives. *Intern. J. Biol. Macromol.*, in press.

Bataille I., D. Charpentier, J. Huguet, L. Merle, G. Muller, G. Mocanu and A. Carpov (1996), Nouveaux polysaccharides chargés associatifs à base de cellulose et de pullulane. *Synth. Polym.*, Ed. Romanian Polymer Society, in press.

Final manuscript received in January 1997