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PROPERTIES OF ACRYLIC ASSOCIATIVE THICKENERS

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INTRODUCTION

Hydrophobically associative polymers are well known for their strong thickening properties in aqueous solutions. They are classically used in coatings, cosmetics but could be considered for different petroleum applications such as drilling fluids or cements. With this aim, extensive studies have been performed on hydrophobic acrylic derivatives to obtain a whole comparison of their behaviour with conventional water soluble polymers. A detailed methodology has been designed to determine polymer molecular weight by light scattering in a proper choice of solvent to minimize hydrophobic interactions. Studies of polymer solution properties in different ionic environments, thermal stability and adsorption behaviours on well characterized minerals has been conducted. Introduction of hydrophobic moieties on hydrophilic polymer chains leads to polysoaps and induces the formation of specific polymer/polymer interactions that affect all polymer properties, in particular specific resistance to high ionic strength or thermal degradation.

1 MATERIALS

The associative polymers used in this study are presented in Figure 1. They are copolymers of sodium acrylate and butylacrylate, presenting 20% of hydrophobic moieties for ABA 1 and 45% for ABA 2. These polymers are classically commercialized for painting formulations and presented as a 40% concentrated solution at neutral pH for ABA 1 and as a 32% emulsified form at acid pH for ABA 2. The latter has to

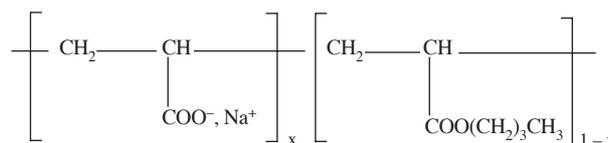


Figure 1

Structure of the acrylic associative thickener (ABA 1 $x = 0.8$, ABA 2 $x = 0.55$).

be inverted at pH 9 so that the polymer develops its viscosity. The molecular weight determination was performed in electrolyte solutions such as LiCl solutions where polymer/polymer interactions are modified due to salting-in effects [1] (see Table 2). For charged polymers such as ABA 1 or ABA 2, there is a competition between the screening of negative charges and the modification of solvent conditions for the hydrophobic moieties. The polymer solutions have been progressively dialysed against LiCl solutions 1M then 2M in order to obtain homogeneous solutions. Molecular weight is respectively 17.10^3 and 8.10^6 for ABA 1 and ABA 2. The behaviour of these two polymers was compared to a partially hydrolysed polyacrylamide acrylic acid with a Mw 8.10^6 and 30% of acrylate content. Adsorption measurements were performed on a bentonite sample provided by the *Société Française des Bentonites* that is a quite pure Wyoming-montmorillonite [2] and [3].

2 EXPERIMENTAL PROCEDURE

Polymer solution concentrations were determined using a total carbon analyser Shimatzu TOC 5050. The polymer solutions were then used as such or dialysed against water

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through a membrane having a molecular weight cut-off of 10.000 or 1000 depending on the molecular weight. Dialysis was continued as long as some carbon impurities were detected in the effluents. This corresponds to the elimination of some surfactant molecules which are not directly bound to hydrophobic moieties. Some polymer solutions have been obtained after polymer precipitation in isopropyl alcohol and dissolution in deionised water. The different ways of purification affect the polymer solution behaviour as presented in the part "Solution behaviour". Polymer solutions were characterized at low shear rates using a Contraves low shear 30. The adsorption measurements and thermal stability tests were performed using the experimental methodology previously described [1] and [4].

3 RESULTS AND DISCUSSION

3.1 Solution behavior

In KCl 5 g/l, polymer intrinsic viscosity and Huggins constant are respectively equal to 14.8 cm³/g, 0.4 for ABA 1 and 200 cm³/g, 2.3 for ABA 2. Due to its high butylacrylate group content ABA 2 behaves like a polysoap as previously described [5] presenting a high level of chain compacity. The high *k'* value indicates a strong associative tendency of polymer chains.

3.1.1 Influence of solution purification

The surfactant used in the polymerization process is a derivative of ethoxylated nonylphenol and its content can be determined by UV spectroscopy at 392 nm. Polymer characteristics are given in Table 1. Only precipitation and extensive washing lead to a strong decrease in surfactant content. This is correlated to the decrease in intrinsic viscosity and increase in Huggins constant both indicating enhancement of polymer intra and intermolecular associations. But after such a process, the rehydration of polymer molecules is very difficult and polymer chains are strongly aggregated [6] and [7]. As previously observed [6], dialysis induces elimination of some surfactant molecules bound to polymer molecules.

TABLE 1

| ABA 2 characteristics in KCl 5 g/l | [η] cm ³ /g | <i>k'</i> | (%) surfactant |
|------------------------------------|-------------------------------|-----------|----------------|
| raw | 200 | 2.3 | 5 |
| dialysed | 250 | 9.2 | 3.8 |
| precipitated, washed and dried | 100 | 3.5 | 1.2 |
| precipitated | 240 | 1.8 | 3.4 |

3.1.2 Influence of ionic content

The influence of different ionic environments was studied on ABA 2 solution behaviour and compared to HPAM behaviour. Results are presented in Table 2. With increasing salt content, the hydrodynamic volume of HPAM chains decreases due to the screening of electrostatic repulsions. Intrinsic viscosity of ABA 2 is slightly affected by increasing salt content but as previously observed intermolecular polymer/polymer interactions are enhanced by salting-out effects [8].

Contrary to HPAM, no precipitation is observed in presence of calcium for ABA 2 polymer. Moreover, intermolecular associations are predominant as a function of time. It seems that there is a balance between the electrostatic interactions and the hydrophobic interactions leading to a reequilibrium among the solutions with time. Fe-II induces attractive interactions between HPAM polymer chains [4] as indicated by the increase of [η]. For ABA 2, these interactions are mainly intermolecular correlated with the increase in Huggins constant.

TABLE 2

| Electrolyte | HPAM | | ABA 2 | |
|---|-------------------------------|-----------|-------------------------------|-----------|
| | [η] cm ³ /g | <i>k'</i> | [η] cm ³ /g | <i>k'</i> |
| LiCl 2M | – | – | 140 | 0.3 |
| KCl 5g/l | 7200 | 0.3 | 200 | 2.3 |
| KCl 30g/l | 2600 | 0.7 | 180 | 3.6 |
| KCl 5g/l-CaCl ₂ 1g/l, t=0 | 3900 | 0.3 | 160 | 1.6 |
| KCl 5g/l-CaCl ₂ 1g/l, t=36 hours | phase separation | | 110 | 3.3 |
| KCl 5g/l + FeCl ₂ 3 ppm | 10 000 | 0.6 | 240 | 8.5 |

3.2 Thermal stability

Comparison of HPAM, ABA 1 and ABA 2 behaviours is given in Table 3. Ageing was performed at the indicated temperature and the solution characterization at room temperature. HPAM is more and more hydrolyzed with temperature. Molecular weight degradation induces an easier accessibility of OH⁻ to polymer chains and thus a higher hydrolysis degree than expected. Both ABA 1 and ABA 2 structures are slightly affected by temperature with a limited hydrolysis of butylacrylate groups. For ABA 2 which presents the higher hydrophobic group content, viscosity strongly evolves after ageing with temperature leading to an enhancement of intermolecular associations at 90°C. After ageing at 140°C, hydrophobic associations are probably so strong that the structure is very compacted and the solution contains some aggregates that will not be soluble. A decrease in viscosity is then observed.

TABLE 3

| Polymer characteristics KCl 5 g/l | HPAM | ABA 1 | ABA 2 |
|--------------------------------------|------------|------------|-----------|
| Initial | | | |
| $[\eta]$ cm ³ /g - k' | 7200 - 0.3 | 14.8 - 0.4 | 200 - 2.3 |
| acrylic % | 30 | 80 | 55 |
| 90°C - 24 hours | | | |
| $[\eta]$ cm ³ /g - k' | 5000 - 0.4 | 12.8 - 0.7 | 230 - 5.9 |
| acrylic % | 35 | 81 | - |
| 140°C - 24 hours | | | |
| $[\eta]$ cm ³ /g - k' | 1000 - 0.4 | 12 - 0.7 | 550 - 0.8 |
| acrylic % | 90 | 88 | 55 |

3.3 Adsorption behavior

As previously observed with acrylamide/nonylmethacrylate copolymer [1], both ABA 1 and ABA 2 present a non classical adsorption isotherm with an increase of polymer adsorption with polymer solution concentration (Fig. 2 and 3). This has been attributed to the formation on the surface of multilayers composed of polymer chains directly bound to the surface and chains interacting by hydrophobic associations with polymer chains directly bound to the surface. The effect is particularly important for ABA 1 polymer that presents the lower molecular weight but a level of adsorption at the same salinity closed to a classical polyacrylamide of very high molecular weight [3]. Comparison of adsorption isotherms seems to indicate that the length of the adsorption plateau corresponding to a mono layer is probably molecular weight and hydrophobic content dependent. This has to be further studied as well as the influence of the repartition of the hydrophobic groups onto the polymer chains.

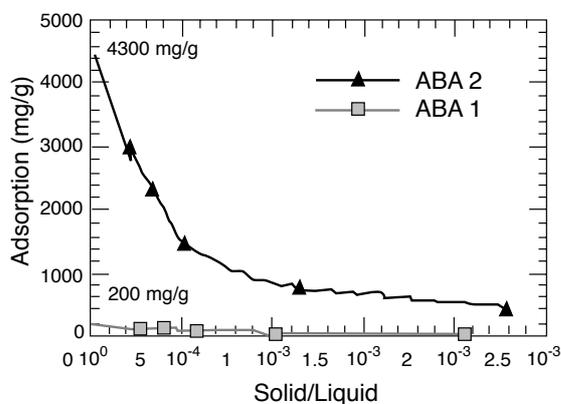


Figure 2
Adsorption of ABA 1 and ABA 2 on K-montmorillonite in KCl 20 g/l.
Influence of the solid/liquid ratio (S/L).

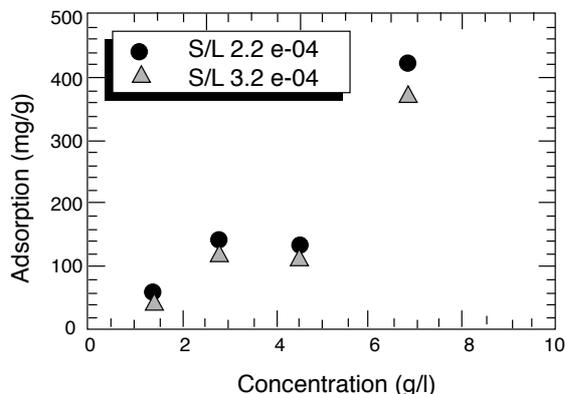


Figure 3

Adsorption isotherms of ABA 1 on K-montmorillonite in KCl 20 g/l.

CONCLUSIONS

Extensive studies have been performed on hydrophobic acrylic derivatives to obtain a whole comparison of their behaviour with conventional derivative of acrylic acid/acrylamide copolymer, in particular, concerning polymer solution properties in different ionic environments, thermal stability, adsorption behaviours on well characterized minerals. Introduction of hydrophobic moieties on hydrophilic polymer chains leads to polysoap polymer behaviour and induces the formation of specific polymer/polymer interactions that affect all polymer properties, in particular specific resistance to ionic contents or thermal degradation and specific adsorption behaviour.

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