EFFECT OF XANTHAN GUM AND SODIUM CARBOXYMETYLCELLULOSE ON THE RHEOLOGICAL PROPERTIES AND ZETA POTENTIAL OF BENTONITE SUSPENSIONS

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Résumé

L'utilisation de polyélectrolytes anioniques pour contrôler la stabilité et le comportement de floculation de suspensions colloïdales est d'une grande importance technologique. Ils sont largement utilisés dans divers produits industriels, tels que les peintures, les revêtements, les céramiques, les pesticides, les produits pharmaceutiques, les cosmétiques et les fluides de forage, pour modifier la rhéologie et contrôler la stabilité des systèmes. Des mesures rhéologiques en mode d'écoulement sont obtenues à partir de viscosimètre à cylindre coaxial couvrant une large plage de vitesse de cisaillement (0 à 700 s^{-1}), pour mettre en évidence l'effet de deux polyélectrolytes anioniques tels que la gomme xanthane et la carboxyméthylcellulose sodique (Na-CMC) sur les propriétés rhéologiques de la suspension de bentonite. Des essais rhéologiques de la suspension de bentonite, des solutions aqueuses de polyélectrolytes et des mélanges polyélectrolytes-bentonite sont largement étudiées. La loi de Herschel-Bulkley a été utilisée pour l'ajustement des courbes d'écoulement de divers échantillons de suspension de bentonite dont la concentration en solide varie entre 3 et 6%, le coefficient de corrélation > 0,997 pour l'ensemble du système étudié. Les résultats obtenus ont montré que la contrainte seuil et l'indice de consistance augmentent avec l'augmentation de la concentration en bentonite, d' autre part, les valeurs de l'indice d'écoulement diminuent. Pour évaluer l'influence des polyélectrolytes sur la suspension de bentonite, les essais rhéologiques ont été effectués sur les solutions de polyélectrolytes en l'absence de bentonite. Le comportement rhéologique des solutions de xanthane est de type non-newtonien à seuil. Les courbes d'écoulement sont également modélisées par la loi de Herschel-Bulkley, toutes les courbes d'écoulement ont été ajustées avec un coefficient de corrélation > 0,99. On *constate que la contrainte seuil (1,048-5,264 Pa) et l'indice de consistance (0,06-0,67) augmentent avec l'augmentation de la concentration du polymère. Par contre, l'indice d'écoulement (0,68-0,45) diminue légèrement. Il a été montré que la présence de carboxyméthylcellulose dans la suspension de bentonite a permis d'éliminer la contrainte seuil et d'augmenter la viscosité du mélange. D'autre part, le xanthane a induit une augmentation de la contrainte seuil et une augmentation élevée de la viscosité des mélanges bentonite-polymère. Les mesures électrocinétiques montrent une augmentation du potentiel zêta des dispersions de CMC et de xanthane lorsque la concentration de polymère en solution augmente. Les valeurs de potentiel zêta du mélange bentonite-polyélectrolyte sont affectées par la nature du polyélectrolyte.*

Abstract

The use of anionic polyelectrolytes to control the stability and flocculation behavior of colloidal suspensions is of great technological importance. They are widely used in various industrial products, such as paints, coatings, ceramics, pesticides, pharmaceuticals, cosmetics, and drilling fluids, to modify the rheology and control the stability of systems. Experimental flow measurements, obtained by coaxial cylinder viscometer covering a wide range of shear rate (0 to 700 s^{-1}), were used to highlight the effect of two anionic polyelectrolytes such as, xanthan gum and sodium carboxymethylcellulose (Na-CMC) on the rheological properties of the bentonite suspension. The rheological measurements of bentonite suspension, polyelectrolytes aqueous solutions, and mixture bentonite-polyelectrolytes are extensively investigated.

Firstly, Herschel-Bulkley law was used for fitting flow curves of various samples of bentonite suspension whose the concentration in solid varies between 3-6 %, the regression coefficient > 0.997 for all studied system. The obtained results showed that the yield stress and the consistency index increase with increasing bentonite concentration, on the other hand, the flow index values decrease. To asses the influence of polyelectrolytes on bentonite suspension, the rheological tests have been carried out on the polyelectrolytes solutions in absence of bentonite. The rheological behavior of xanthan solutions is shear-thinning non-Newtonian viscosity with yield stress. The flow curves are also modeled by Herschel-Bulkley law, all flow curves have been fitted with a correlation coefficient > 0.99. We note that the yield stress (1.048-5.264 Pa) and the consistency index (0.06-0,67) rise with the increase in polymer concentration, By cons, the flow index (0,68-0,45) decreases slightly. It has been shown that the presence of carboxymethylcellulose in the bentonite suspension has helped to remove the yield stress and to increase the viscosity of the mixture. On the other hand, the xanthan induced an increase in the yield stress and a high increase in viscosity of the bentonite-polymer mixtures. The electrokinetic measurements show an increase of the zeta potential of CMC and xanthan dispersions when the concentration of polymer in solution increases. The values of zeta potential of mixture bentonite-polyelectrolyte are affected by the nature of polyelectrolyte.

Keys words: CMC, Xanthan, rheology, zeta potential

1 INTRODUCTION

Polymers, such as cellulose derivatives [1,2,3], biopolymers [4,5,6] and guar gum [3,6] were introduced in the water based drilling fluids for their rheological performance and for ecological considerations. In comparison with other natural polymers, the cellulose derivative is the most used because it is biodegradable and compatible with other materials. Carboxymethylcellulose (CMC) is produced by reacting cellulose obtained from wood pulp or cotton fibers with chloroacetic acid and NaOH. The presence of polar carboxyl groups makes the cellulose soluble, chemically reactive and strongly hydrophilic [7]. CMC is a white to almost white powder, non-toxic and biodegradable, odorless and does not ferment under normal conditions of use. It is also a low-cost commercial soluble and it can be dissolved in hot or cold water. It is largely used in industry, due to its exceptional rheological properties in aqueous solutions. It is also employed as an additive in food industry [8,9] and pharmaceuticals. The rheological properties of CMC depend of the concentration in polymer and the degree of substitution which varies from 0.5 to 1.2. Aqueous solutions of CMC are stable at pH 2 to 10. Precipitation can occur below pH 2, and solution viscosity decreases rapidly above pH 10. Generally, solutions exhibit maximum viscosity and stability at pH 7 to 9. CMC is regarded as a polyelectrolyte, once it is dissolved in water, the Na-CMC molecule is separated into sodium cations and into anionic polymer.

2 Materials and Equipment

The clay used is a drilling bentonite from Maghnia (west of Algeria). Its reserves are considered to be the largest in the world. The chemical composition of this bentonite is shown in Table 1. It consists mainly of montmorillonite, which is the predominant mineral clay. Other minerals, such as quartz, illite, and feldspar residues, are also present. The additives used are as follows:

(a) Xanthan gum is a polysaccharide anionic product in an industrial scale obtained by the aerobic fermentation of the bacteria Xanthomonascampestris. It shows some stability to temperature, salinity, and pH [2, 5]. The role of xanthan is to improve the viscosity of the drilling mud.

(b) CMC is a molecular chain that is derived from cellulose. Depending on the degree of substitution and molecular weight, the CMC aqueous solution is presented in three forms: large, medium, and low viscosity. In a drilling mud, the CMC is a viscosifiant, but mostly it plays the role of a reducer of filtrate.

All rheological measurements have been made using a VT550 rotational viscometer. This apparatus was equipped with concentric cylinder geometry of outer radius of 21 mm and gap width of 1.64 mm. The shear rates were in the range 0 to 600 s^{-1}. The temperature is kept constant at 20°C during all measurements. In order to avoid problems of evaporation during handling, the measuring device was placed in an environment saturated with water.

The electrokinetic tests of bentonite-polymer were measured with an automated electrophoresis instrument (Zétasizer 2000, Malvern Instruments Ltd., Malvern, UK) equipped with a microprocessor unit. The unit calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation as follows:

$$\zeta = \frac{4\pi V_t}{D_t} \times EM$$

Where EM is electrophoretic mobility at given temperature, V_t is viscosity of the aqueous medium, D_t is dielectric constant, π is constant and ζ is zeta potential.
Each zeta potential value is the average of five data, using standard deviation like experimental error of measurements.

3 Results and discussion

3.1 Rheological measurement

3.1.1 Bentonite-xanthan mixture

The results of flow test of different mixtures of bentonite (5%) xanthane (fig.1) at various concentration of xanthan show that the shape of the rheogramm is similar to the solutions of xanthan. We note that the apparent viscosity and the yield stress increase with the xanthan concentration. The presence of polymer conduct to improve the two rheological parameters, the viscosity and the yield stress.

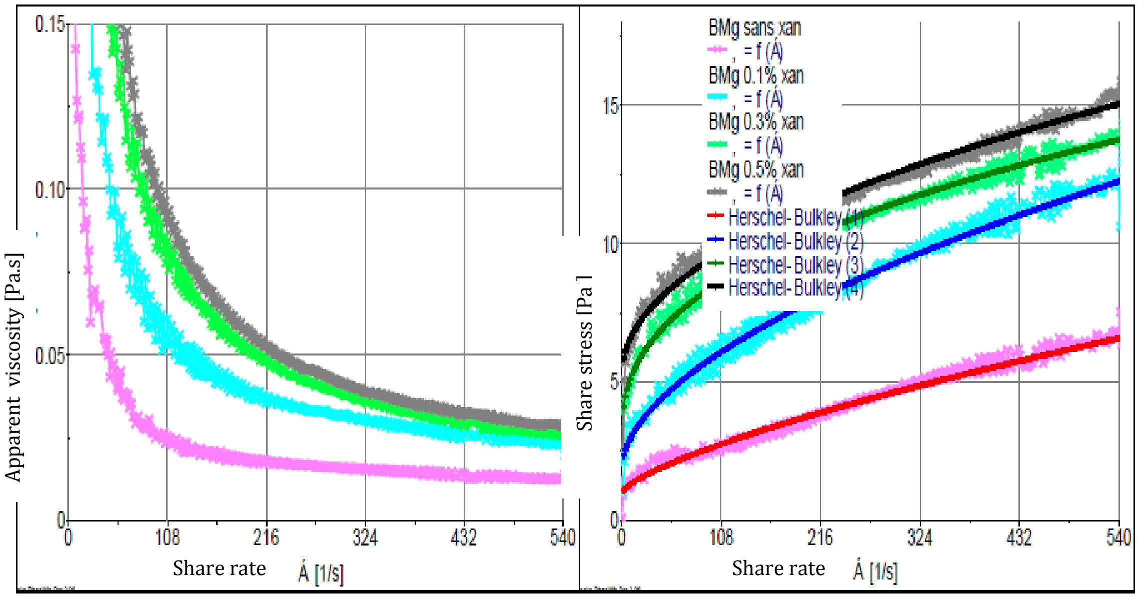

Fig.1 Effect of xanthan on the rheological behavior of bentonite suspension at 5%

According to (Benyounes et al., 2010) [1], this confirms that the rheological behavior of the polymer solution predominates that of the clay suspension. In this case, the macroscopic behavior of the bentonite-xanthan mixtures is controlled by xanthan.
Furthermore, the flow curves of the bentonite-xanthan mixture can be fitted using the Herschel-Bulkley model [Eq. (1)].

$$\tau = \tau_0 + k.\dot{\gamma}^n \qquad (1)$$

The rheological parameters are summarized in Table 1. One can notice that for the bentonite-xanthan mixture, the yield stress and consistency, k, increase with the xanthan concentration. In contrast, the flow index, n, decreases with the polymer concentrations, which lead to a flow behavior closer to that of xanthan solution. In fact, the presence of xanthan in the mixture allows reinforcement of the rigidity and the consistency of the mixture because of the structural nature of the xanthan. A literature survey indicates that when a macromolecule is adsorbed on a clay surface, the connection between particles is allowed. The adsorption increases the load on the surface of the particle and consequently gives a more dispersed system. This leads to an increase in the zeta potential and amplification of the forces of repulsion between clay particles. It is the structural nature of the polymer and its adsorption on the clay particles that cause the change of the rheological behavior and stability of the mixtures [10].

On the other hand, the basic nature of mixtures is also noticed. In this case, the faces and edges are of negative charge [11]. Therefore, any electrostatic interaction hypothesis, usually assumed between anionic charges of the polymer and positive charges of the edges of clay particles, can be put aside. Thus, the mechanism of interaction clay-polymer is summed up in the forces of van der Waals and the hydrogen bonding. The hydrogen bonds are built between the hydrogen and the hydroxyl of clay and those of the groups D-glucoronic, D-mannose, and pyruvate of the xanthan molecule. We believe in the relevance of such a hypothesis for bentonite-xanthan mixtures, especially that the concentration of clay is sufficiently small, to consider a dominant polymer-polymer contact. The results of this study confirm that the rheological behavior of polymer solution is the dominant one in the bentonite-xanthan mixtures.

Table 1 Rheological parameters of the Herschel-Bulkley model for the bentonite-xanthan mixtures

	Compositions %			**Rheological parameters**			
Formulations	Water	Bentonite	*XAN*	τ_0	K	n	r
BMg without XAN	95	5	*0*	1.048	0.057	0.725	0.9881
BMg 0.1% XAN	94.9	5	*0.1*	1.930	0.284	0.565	0.9905
BMg 0.3% XAN	94.7	5	*0.3*	**3.017**	0.856	0.402	0.9914
BMg 0.5% XAN	94.5	5	*0.5*	**5.264**	0.439	0.493	0.9929

3.1.2 Bentonite-CMC mixture

The effect of adding CMC on the rheological properties of the bentonite suspension is shown in Figure 2. An increase in apparent viscosity according to the concentration of CMC is observed. This is due to the number of entanglements caused by long polymer chains. To equal shearing, and for the same concentration of polymer, the apparent viscosity of the bentonite-CMC mixture is still higher than the viscosity of the bentonite suspension. The disappearance of the yield stress on all bentonite-CMC mixtures is also noticed. In addition, the shapes of bentonite (3%)-CMC mixtures flow curves (Figure 2) are similar to those reported on bentonite-CMC mixtures and of CMC solutions, by Benyounes et al., 2007 [12]. All flow curves in Figure 2 exhibit a shear-thinning behavior and can be correlated by the Cross model as reported in the literature on bentonite-CMC mixture and CMC solutions [12].

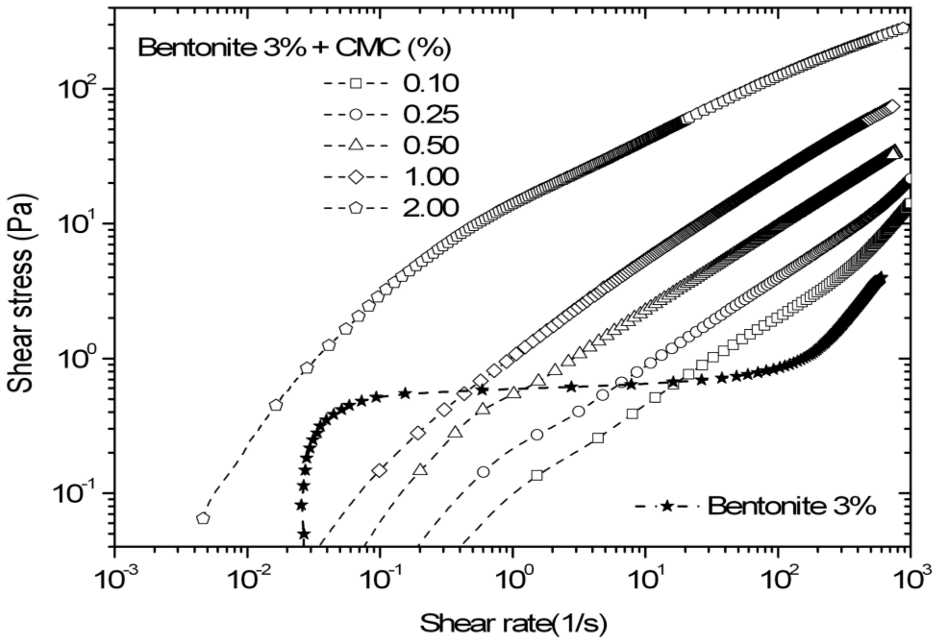

Fig.2 Flow curves of bentonite-CMC mixtures.

3.2 Zeta potential measurement

The dispersion of bentonite- xanthan solution has a zeta potential value -42 mV in comparison to bentonite-CMC which has a value of -32mV, this shows that the mixture are very stable [13].The negative charge of mixture is generally believed to be due to the dissociation of Na+ from carboxylic groups.

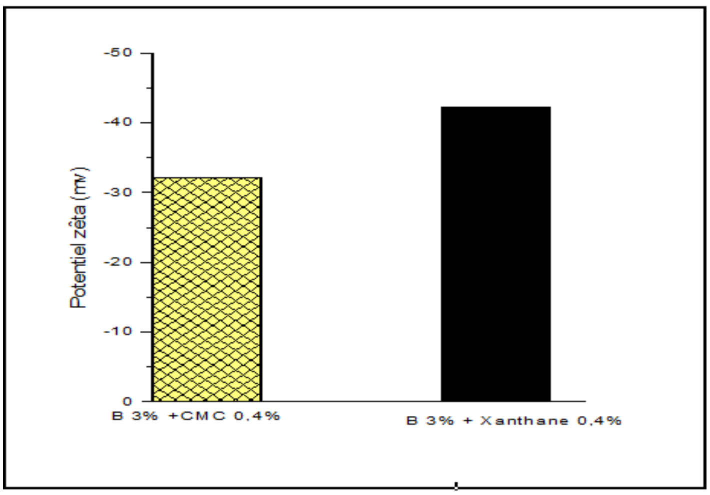

Fig.3 Zeta potential of bentonite-polymer

3 Conclusion

The rheological properties of bentonite suspension, and the influence of the presence of xanthan and CMC on the rheological behavior of a bentonite suspension have been investigated. The rheological measurements have shown that the suspension of bentonite have revealed a yielding behavior. The rheological behavior can be described adequately by the model of Herschel-Bulkley; The different rheological measurements on bentonite-polymers blends have revealed clearly the effect of xanthan gum and CMC on the rheological properties of bentonite suspension. The presence of xanthan in the mixtures leads to the increase of the yield stress and the viscosity of bentonite suspension. The same observations were also made for the bentonite-CMC mixtures with an absence of the yield stress. This is due to the chemical structure of CMC, which allows the dispersion of the clay particles. The electrokinetic study of bentonite-polymer blends showed the stability of these mixtures

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