



## Research paper

## Use of Carbopol 980 and carboxymethyl cellulose polymers as rheology modifiers of sodium-bentonite water dispersions

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## ABSTRACT

The effects of polymer addition on the rheological parameters of sodium bentonite water dispersions at ambient conditions were studied using high molecular mass carboxymethylcellulose (CMC) and Carbopol 980. Adsorption isotherms using the batch equilibrium technique of the polymers onto the bentonite particles were Langmuir isotherms of the L1 type, indicating monolayer adsorption of the polymers onto the surface of the bentonite particles. The aqueous dispersions of 3% and 4% sodium bentonite exhibited Herschel–Bulkley rheological behavior. Addition of CMC up to 1.5% by mass to the 3% sodium bentonite dispersions decreased the yield stress and the flow consistency index because of the steric effects caused by the adsorption of the polymer. This state was then followed by a plateau of the yield stress and a considerable increase of the flow consistency index, indicating that after a particular polymer concentration, further addition merely increased the liquid viscosity of the mixture. The flow behavior index was not affected by CMC addition. Addition of Carbopol 980 to the 3% and 4% sodium bentonite dispersions up to 0.15% by mass again firstly decreased the yield stress and the flow consistency index, then increased the yield stress and the flow consistency index with increasing polymer concentration. The high shear viscosity of bentonite–Carbopol dispersions showed also a minimum followed by a drastic increase. The flow behavior index was not affected significantly by the polymer addition.

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## 1. Introduction

Due to the colloidal and rheological properties, bentonites find a wide variety of applications in various industries like wastewater treatment, ceramics, cement, paint, paper and drilling fluids. Drilling fluids are extremely important for the oil, gas and geothermal drilling industry as they are the blood of the well. They are used to transport the rock cuttings to the surface, to lubricate the drill bit, to prevent fluid loss into the formations and to apply hydrostatic pressure in the well bore (Darley and Gray, 1998; Hughes et al., 1993; Kelessidis et al., 2007a). Severe conditions encountered while oil-well drilling in deep-horizons, in horizontal and near horizontal wells demand complex formulations of drilling fluids. Continuous demand for hydrocarbons pushes the industry to drill in deep horizons, often exceeding 5000 m with high temperatures which may cause gelation of bentonite dispersions. In order to avoid such problems, different additives and particularly a variety of polymers like cellulose, guar gum, xanthan gum, polyacrylates and polyacrylamides are used for controlling the viscosity and the yield stress of drilling fluids as well as to reduce formation damage (Kelessidis et al., 2007b; Liu, 2007; Luckham and Rossi 1999; Rossi et al., 1999). The use of polymers allows control of

flocculation and deflocculation behavior of bentonite dispersions, reduces excessive friction and increased torque while at the same time imparts low impact on the environment compared to oil-based drilling fluids (Dolz et al., 2007; Isci et al., 2004; Mahto and Sharma, 2004).

A polymer commonly used by drilling fluid industry is carboxymethylcellulose (CMC) with a wide range of uses in paper industry, in food products, in pharmaceuticals and in drilling fluids. In the oil industry, the high water retention of CMC promotes the stabilization of the aqueous dispersion of bentonite based drilling fluids. It can increase the viscosity of the drilling fluid and reduce fluid losses to the formation (Amorim et al., 2007; Benhabane and Bekkour, 2006; Darley and Gray, 1998; Iscan and Kok, 2007). CMC is a highly charged anionic polyelectrolyte with carboxylic acid groups. It is the reaction product of cellulose with sodium hydroxide and chloroacetic acid (Edali et al., 2001). The polymer chain of CMC in solution is partly in a helical conformation which considerably influences the rheological behavior of CMC in aqueous solution (Yasar et al., 2007). The temperature and particularly the concentration of CMC have significant impact on the rheological behavior of its dispersions (Pilizota et al., 1996). Each polymer chain in a diluted solution of CMC is hydrated and extended, and the solution then exhibits stable viscosity (Gómez-Díaz and Navaza, 2002). CMC addition causes steric stabilization to bentonite dispersions (Lagaly, 2006; Lagaly and Ziesmer, 2003). Studies of the rheological behavior of bentonite–CMC dispersions have been reported by Menezes et al. (2010), Singh and Sharma (1991), and Singh et al. (1992).

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Carbopol polymers are water soluble vinyl polymers consisting of chains of cross-linked poly(acrylic acid). Their solutions often exhibit a yield stress and are widely used for making emulsions, for thickening and gelation in many industries (Tabuteau et al., 2007). They are not used as additives by drilling fluids industry. The exact structure of Carbopol is not readily available and depends on the type of Carbopol. Their aqueous solutions have pH in the range of 2.5 to 3.5 when dissolved in water. The addition of a base is required to reach the typical yield stress and weak gel behavior (Curran et al., 2002).

Although CMC is used extensively in the formulation of drilling fluids, there are few publicly available rheological or adsorption studies. The effect of Carbopol on the rheological behavior of drilling fluids was not studied. The aim of this study was to investigate the influence of CMC and Carbopol addition on the rheological behavior of sodium bentonite dispersions and to determine the mode of adsorption of these polymers onto the bentonite particles.

## 2. Materials and methods

### 2.1. Materials

Wyoming sodium bentonite was obtained from Halliburton-Cebo Holland. This bentonite is used in drilling fluids. The particle size distribution (Fig. 1) is centered around 8  $\mu\text{m}$ . The cation exchange capacity (CEC) of this bentonite was 0.70 meq/100 g bentonite (Kelessidis et al., 2007a). Carboxymethylcellulose as a sodium salt with the molar mass of 250,000 and with the degree of substitution of 1.2 was obtained from Sigma Aldrich. Carbopol 980 was provided by Noveon.

The preparation of the dispersions for the rheological experiments was carried out following the American Petroleum Institute standard (2006) which was shown to give consistent results from batch to batch (Kelessidis et al., 2007a,c). It involved the mixing in a special mixing cup of 500 ml of deionized water with the desired quantity of bentonite. The mixture was continuously agitated for 20 min using a Hamilton Beach mixer at 11,000 rpm and was left in a covered container for 16 h at room temperature for complete hydration. The sample was stirred for 5 min prior to the rheological measurements.

The CMC only solutions were prepared similarly. The time needed for the hydration was 2 h. The preparation of Carbopol solutions was different to ensure consistent results (Kelessidis and Chatzistamou, 2011). After hydration, the bentonite dispersion and either of the polymer solutions at the predetermined concentrations were mixed in equal proportions for 10 min in order to ensure that they were completely mixed.

### 2.2. Methods

The viscometric data were acquired with a concentric cylinder Couette viscometer from Grace Instruments (USA), with a gap size of 0.117 cm (Kelessidis et al., 2007a). The measurements were done at

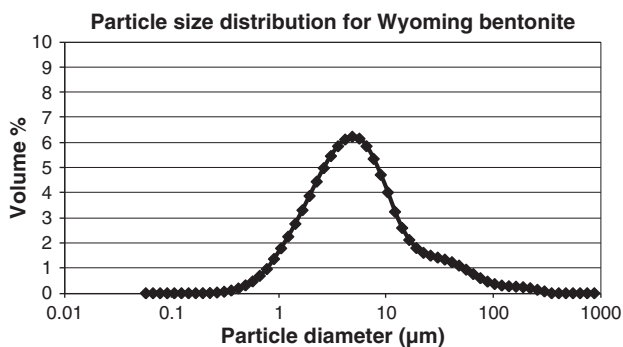


Fig. 1. Particle size distribution of Wyoming bentonite.

fixed speeds of 600, 300, 200, 100, 6, and 3 rpm starting from high to low shear rates. The time of measurement at each speed was 60 s taking six measurements and averaging to get the shear stress value at each rotational speed. All measurements were performed at an average temperature of 23 °C. All data, with the exception of the pure CMC solutions, were fitted by the Herschel–Bulkley model (Dolz et al., 2007; Kelessidis et al., 2006, 2007a; Power and Zamora, 2003; Rossi et al., 2003)

$$\tau = \tau_y + K \cdot \dot{\gamma}^n \quad (1)$$

where  $\tau$  is the shear stress,  $\dot{\gamma}$  the shear rate,  $\tau_y$  the yield stress,  $K$  the flow consistency index and  $n$  the flow behavior index. Newtonian shear rates were used making the narrow gap assumption although this approach was recently questioned (Kelessidis and Maglione, 2008a). The values of the Herschel–Bulkley rheological parameters were determined by the procedure proposed by Kelessidis et al. (2006). The yield stresses reported in this work, determined by extension of the rheogram and the curve fitting, are deemed the true yield stresses of the materials tested as it was shown before (Kelessidis and Maglione, 2008b). The rheological behavior of the bentonite free, CMC dispersions was described well by the power law model (Benchabane and Bekkour, 2006; Muller and Davidson, 1994) given by

$$\tau = K_p \cdot \dot{\gamma}^{n_p} \quad (2)$$

where  $K_p$  is the flow consistency index and  $n_p$  the flow behavior index for the power law model.

The adsorption isotherms were obtained using the batch equilibrium technique. After preparation the dispersions were stirred for 24 h to avoid time-dependent changes. Aliquots of the solution were then centrifuged at 11,400 rpm for nearly 1 h and analyzed with a UV–Visible spectrophotometer (DR/4000 U spectrophotometer) at 210 nm. Calibration was performed over polymer concentrations of 0.0 to 1.0% for CMC and 0.0 to 0.15% for Carbopol. The adsorption data for both polymers could be fitted by the Langmuir model

$$q_e = q_m \frac{C_e}{K_L + C_e} \quad (3)$$

where  $q_e$  is the specific amount of polymer adsorbed (mg/g bentonite),  $C_e$  the equilibrium content of the adsorbent in the solution (g/l),  $K_L$  the Langmuir equilibrium constant and  $q_m$  the monolayer capacity of the adsorbent.

## 3. Adsorption of CMC and Carbopol

### 3.1. CMC–bentonite dispersions

Bentonite dispersions were prepared with 3% m/v solid content in demineralized water and the CMC concentrations ranging between 0 and 1.0% m/v. The pH of the bentonite dispersions was 8.90, and no changes were observed when CMC was added. The adsorption data together with the fitting curve are shown in Fig. 2. The Langmuir isotherm was of the L1 type and was given by

$$q_e = 527.9 \frac{C_e}{12.6 + C_e} \quad (4)$$

with a very good correlation coefficient of 0.997 and a sum of square errors of 133.7 (mg/g bentonite)<sup>2</sup>. The range of the determined parameters at the 90% confidence level was for the Langmuir equilibrium constant 392.7 to 662.9 while for the monolayer capacity 7.48 to 17.63. At low concentrations of CMC the adsorbed amount of the polymer increased linearly which means that at these concentrations the polymer was fully adsorbed. With increasing concentration

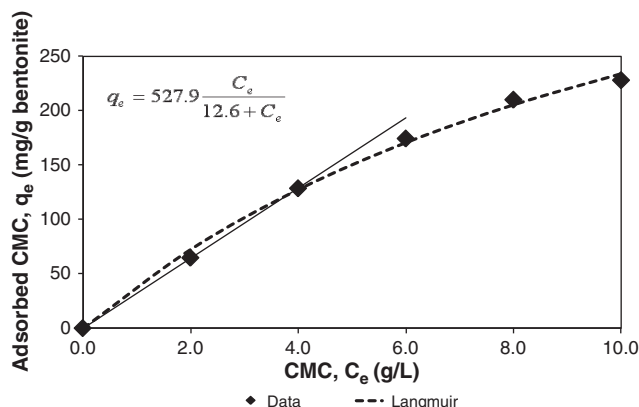


Fig. 2. Adsorption of CMC onto bentonite in 3% bentonite dispersions. The equation for the Langmuir isotherm is also shown. The solid line is shown only to indicate the linear data points.

of CMC, the amounts adsorbed tended to reach a plateau. The amount adsorbed at the maximum concentration tested was then 70% of the equilibrium concentration of CMC. A similar behavior was reported for adsorption of other type of polymers onto bentonite (Rossi et al., 1999, 2003) although these polymers were not ionic. As the Langmuir isotherm described fairly well the data, CMC was adsorbed in monolayers onto the surface of the bentonite particles (Alzaydien, 2009). The maximum amount adsorbed was around 230 mg/g bentonite and this is a similar value to the values reported by Rossi et al. (2003) for non-ionic polymer adsorption on sodium-bentonite and by Alemdar et al. (2005) for poly(ethylamine) adsorption on purified sodium bentonite.

### 3.2. Carbopol–bentonite dispersions

The equilibrium concentrations of Carbopol varying between 0 and 0.15%, the bentonite content of the dispersions was 3% m/v. Addition of Carbopol to the sodium bentonite dispersion decreased the pH from 8.90 to 8.55 at low and to 7.91 at high Carbopol concentrations.

The adsorption data together with the fitting curve are shown in Fig. 3. The Langmuir isotherm was given by

$$q_e = 45.7 \frac{C_e}{1.2 + C_e} \quad (5)$$

with a very good correlation coefficient of 0.999 and a sum of square errors of  $0.19 \text{ (mg/g bentonite)}^2$ . For the data fit, the ranges of the

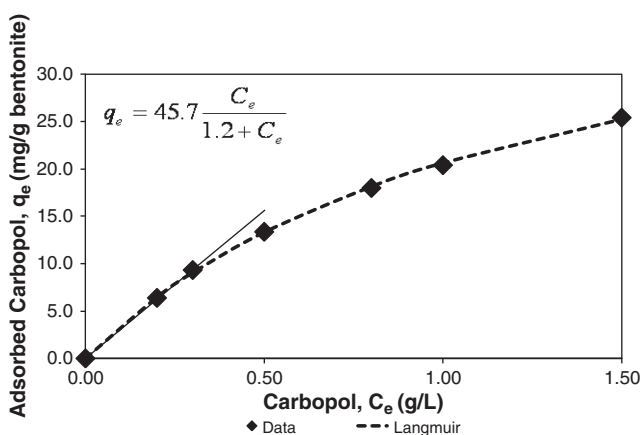


Fig. 3. Adsorption of Carbopol on bentonite in 3% bentonite dispersions. The equation for the Langmuir isotherm is also shown. The solid line is shown only to indicate the linear data points.

determined parameters at the 90% confidence level were for the Langmuir equilibrium constant 43.4 to 47.9 and for the monolayer capacity 1.1 to 1.3. Again the polymer was fully adsorbed at low concentrations and reached the monolayer adsorption at higher concentrations. The amount adsorbed at the maximum tested concentration of 0.15% represented about 50% of the equilibrium concentration of Carbopol in the mixture.

## 4. Discussion

Both polymers showed a high affinity for adsorption onto bentonite particles. Both adsorption curves followed Langmuir isotherm which assumes that there is no interaction between the adsorbate molecules and that no further adsorption can take place when the monolayer coverage is reached (Voudrias et al., 2002). The maximum amount of Carbopol was one order of magnitude smaller than the amount of CMC. As reported by Majzik and Tombacz (2007), the carboxylate groups of the polymers were responsible for the use as the rheology modifiers.

If one calculates the maximum adsorption of the polymers on the basis of the content of the carboxylate groups, the adsorption efficiency is of similar order of magnitude. For example, Carbopol has on average a molar segment mass of 76 per carboxyl group (Hosmani, 2006) while monosubstituted CMC has an average molecular mass 242 per carboxyl group (FAO, 1967). Thus, if the adsorption capacity of bentonite for Carbopol of 45.7 mg/g bentonite is expressed as per carboxyl group, a value of 0.6 mmol of COOH per gram of bentonite is calculated. Similarly, the adsorption capacity of bentonite for CMC of 527.9 mg/g bentonite corresponds to 2.1 mmol COOH per gram of bentonite.

## 5. Rheological behavior

### 5.1. CMC–bentonite dispersions

The power law model described very well the rheological data of the CMC solutions at concentrations of 0.4, 0.8, 1.2, 1.6, and 2.0% m/v. Benchabane and Bekkour (2008) and Benyounes et al. (2007) used the four parameter Cross model to describe the rheological behavior of CMC. However, for the 0.8% CMC solution, the improvement of the correlation coefficient (0.999 versus 0.997) and the small difference of the sum of square errors ( $0.34 \text{ Pa}^2$  versus  $0.65 \text{ Pa}^2$ ) for the Cross and the power model were minimal. Similar differences were calculated for the other concentrations.

Increasing the CMC concentration, the flow behavior index decreased almost linearly from 0.85 to 0.67, which is an indication of the increasing shear thinning behavior of the solution at higher CMC concentrations. There was a large increase of the flow consistency index with the CMC concentration (C), following an exponential type of behavior

$$K = 0.020 \left( e^{1.87C} \right) \quad (6)$$

with a correlation coefficient of  $R_c^2 = 0.996$  and a sum of square errors of  $0.002 \text{ (Pa} \cdot \text{s}^n)^2$ , with the range of parameters at the 90% confidence interval of 0.010 to 0.030 for the constant coefficient and 1.61 to 2.14 for the exponential coefficient in Eq. (6). Our results were in accordance with prior studies where it was reported that CMC solutions exhibited shear thinning behavior and the viscosity at all shear rates increased with increasing CMC concentration (Dapia et al., 2005; Lin and Ko, 1995).

The 3% m/v bentonite dispersions with 0.2–1.0% m/v CMC did not show viscoelasticity (Ghannam and Esmail, 1998). The viscosity of the dispersion as a function of the shear rate is depicted in Fig. 4. All dispersions exhibited Herschel–Bulkley fluid behavior. The viscosity of the polymer–bentonite dispersions at the small polymer concentrations is between the viscosity of the two components, the viscosity

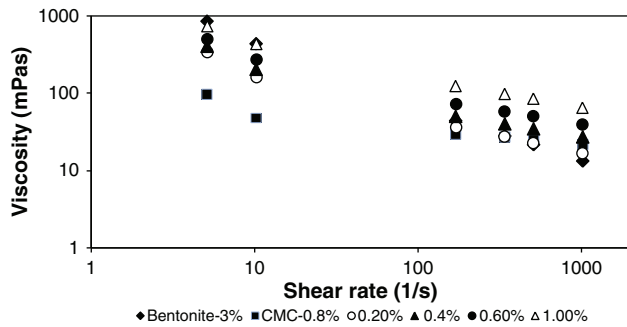


Fig. 4. Viscosity of 3% bentonite–CMC dispersions at various CMC concentrations. The viscosity of the pure 0.8% CMC solution is shown for comparison.

of the pure CMC solution and the viscosity of the pure bentonite dispersion. This is more evident at low shear rates which dictate the values of the yield stress, thus indicating that the yield stress of the bentonite–polymer dispersion will be affected by CMC addition. At higher polymer concentration, the shear stresses at low shear rates approached that of the pure bentonite dispersions. At higher shear rates, the shear stresses are higher than the shear stresses of pure bentonite dispersions but with similar slope, thus indicating an increase of  $K$  and a fairly constant  $n$ . These results become even more evident when the Herschel–Bulkley parameters are presented as a function of the CMC concentration (Fig. 5).

Both the yield stress and the flow consistency index displayed a minimum with increasing polymer concentration then reaching a plateau at a value of about 65% of the polymer-free bentonite dispersion. Similar behavior of the yield stress of bentonite dispersions with CMC addition was reported by Wanko and Bekkour (2003) while Rossi et al. (1997, 2003) reported a constant value of the yield stress when using other polymers. The flow consistency index also showed a minimum with increasing the CMC concentration, then increased in a power law fashion. This increase was similar to the increase of  $K$  of pure CMC solutions (Fig. 5). However, the flow behavior index increased at first with increasing CMC concentration and then remained approximately constant at the values between 0.6 and 0.7 approximating the value of  $n$  of the pure CMC solutions.

## 5.2. Carbopol–bentonite dispersions

The rheological behavior of the Carbopol dispersions was described by pseudoplastic models with a yield stress, and many researchers modeled them as Herschel–Bulkley fluids (Ancey and Cochard, 2009; Curran et al.,

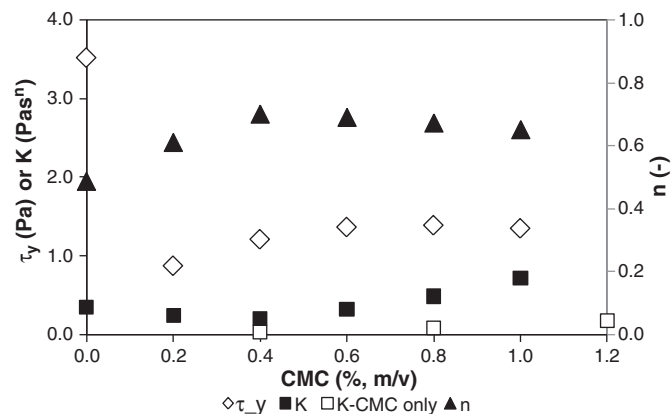


Fig. 5. Yield stress, flow consistency index and flow behavior index of the 3% bentonite–CMC dispersions. The flow consistency index for the pure CMC solution is also shown.

2002). The rheological data of 0.05%, 0.08%, 0.10% and 0.15% were fitted to the Herschel–Bulkley model with very good correlation coefficients  $>0.999$  (Fig. 6). Solutions with  $<0.05\%$  concentration of Carbopol 980 did not exhibit a yield stress as reported earlier (Kelessidis and Chatzistamou, 2011). At higher concentrations, the yield stress increased exponentially with the polymer concentration ranging between 0.0 Pa and 6.5 Pa and could be described by

$$\tau_y = 5756 \cdot (C)^{3.59} \quad (7)$$

where  $C$  is the concentration of the polymer in % m/v,  $\tau_y$  in Pa, with a correlation coefficient of 0.998 and a sum of square errors of  $0.05 \text{ Pa}^2$ . The uncertainty of the coefficients, expressed at the 90% confidence level, was within the range  $-1637$  and  $13,150$  for the standard coefficient, and for the power coefficient within the range 2.92 and 4.26. The flow consistency index varied with concentration as

$$K = 1236 \cdot (C)^{3.38} \quad (8)$$

with  $K$  in  $\text{Pa} \cdot \text{s}^n$ , a correlation coefficient of 0.999 and a sum of square errors of  $0.003 (\text{Pa} \cdot \text{s}^n)^2$ . The uncertainty of the coefficients, expressed at the 90% confidence level, was within the range 347 and 2125 for the standard coefficient, and for the power coefficient was within the range 2.91 and 3.66. The shear thinning behavior as indicated by the value of  $n$  increased with polymer concentration with the flow behavior index approximating a value of about 0.5.

The bentonite–Carbopol dispersions were prepared using two bentonite concentrations, 3% and 4%, while the concentrations of Carbopol 980 varied between 0.02% and 0.15%, as at these low polymer concentrations no viscoelasticity is expected (Roberts and Barnes, 2001). The viscosity of the bentonite–Carbopol dispersions as a function of the shear rate is shown in Fig. 7, together with the viscosity for the pure 0.08% Carbopol solution. At  $<0.10\%$  Carbopol, the viscosity of the bentonite–Carbopol dispersions is between the viscosity of the pure Carbopol viscosity at low shear rates and the viscosity of the pure bentonite dispersions at higher shear rates.

Fitting the data with the Herschel–Bulkley model was excellent for both 3% and 4% bentonite concentrations (Figs. 8–10). The yield stress of the bentonite–Carbopol dispersions also showed a minimum with increasing polymer concentration. The minimum was found at a somewhat lower Carbopol concentration for the 3% bentonite dispersion compared to the 4% dispersion. After the minimum, the increase of the yield stress followed a power law, in a similar way as the pure Carbopol solution. At 0.15% polymer, the yield stress was higher than for the pure bentonite dispersions. The flow consistency index showed also a minimum for the 4% bentonite dispersion while for the 3% bentonite dispersion, the value of  $K$  was small and constant up to 0.05% polymer addition, then increased steeply as in the case of the pure Carbopol solutions. The flow behavior index remained fairly

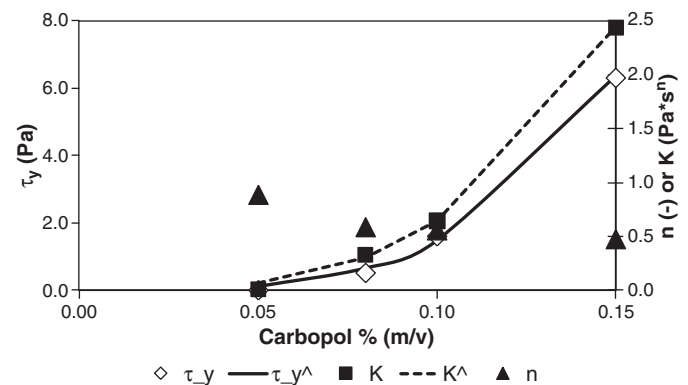


Fig. 6. Herschel–Bulkley rheological parameters of Carbopol solutions.



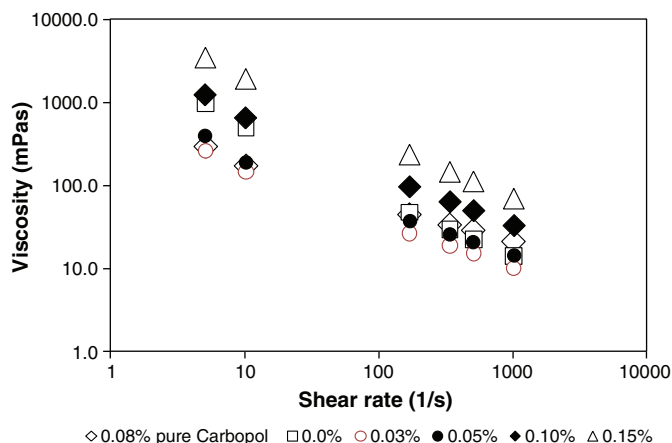


Fig. 7. Viscosity of 3% bentonite–Carbopol dispersions.

constant at about 0.5, close to the value for pure bentonite dispersions. Thus, based on the above analysis, addition of Carbopol to the 3% or 4% bentonite dispersions significantly influenced the yield stress and the flow consistency index, exhibiting minima at polymer concentrations of around 0.05% but not affecting the flow behavior index.

## 6. Discussion

The decrease of the yield stress and the flow consistency index at small amounts of polymer concentrations  $<0.5$  g/l represented the liquefying effect caused by the binding of the polymers onto the bentonite particle surfaces and preventing edge-to-face interaction of bentonite particles. At Carbopol concentrations  $<0.5$  g/l (or 0.05% m/v) (Fig. 3), the polymer was quantitatively adsorbed. At higher polymer concentrations not all polymer molecules were adsorbed thus increasing the yield stress and the flow consistency index. Similar behavior was found for the CMC–bentonite dispersions. For Carbopol, the minimum was observed at 0.05% polymer and 4% bentonite dispersion which corresponded to 0.16 mmol COOH per gram bentonite. For CMC, the minimum was observed at 0.2% polymer and 3% bentonite which corresponded to 0.28 mmol COOH per gram of bentonite.

The constant value of the yield stress of the bentonite–CMC dispersions after the minimum should be seen in relation to the change in the flow consistency index  $K$  which, after the minimum increased in a power law manner, indicating that further addition of the polymer merely increased the liquid phase viscosity and did not affect the way the bentonite particles interact. The high shear viscosity of the 3% bentonite–CMC dispersions (Fig. 11) did not change much at low CMC concentrations but increased steeply after the minimum of the yield

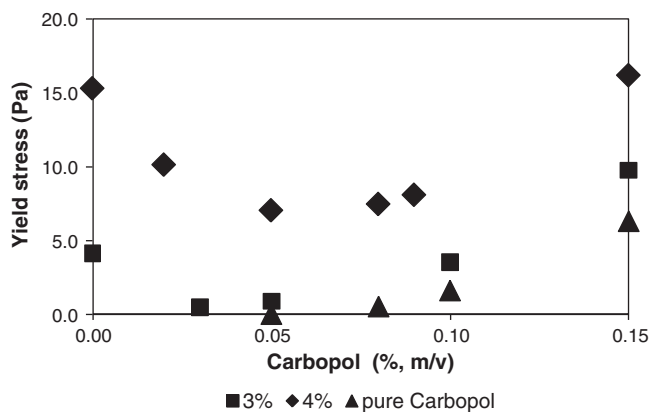


Fig. 8. Yield stress of 3% and 4% bentonite–Carbopol dispersions. The data for pure Carbopol solutions are also shown.

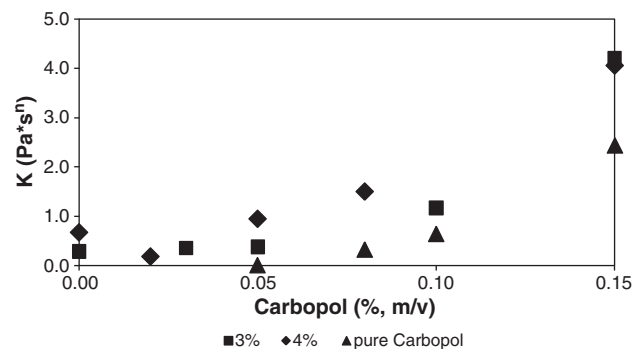


Fig. 9. Flow consistency index of 3% and 4% bentonite–Carbopol dispersions. The data for pure Carbopol solutions are also shown.

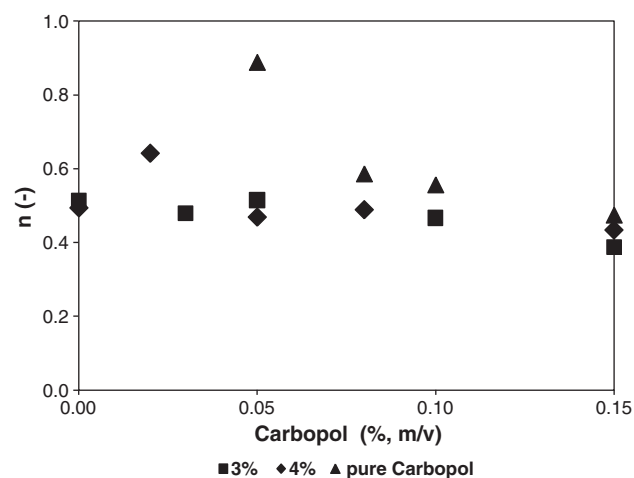


Fig. 10. Flow behavior index of 3% and 4% bentonite–Carbopol dispersions. The data for pure Carbopol solutions are also shown.

stress of bentonite dispersion with 0.2% CMC. For the bentonite–Carbopol dispersions all Herschel–Bulkley parameters increased at polymer concentrations above the minimum because the pure Carbopol solutions also exhibited Herschel–Bulkley behavior. In particular, the yield stress of the dispersion appears to be the summation of the yield stress of the pure bentonite dispersion and of the pure Carbopol solution and this holds for both the 3% and the 4% bentonite concentrations. The high-shear viscosity of the bentonite–Carbopol dispersions (Fig. 11) showed a minimum, as for the yield stress and the flow consistency index, followed by a large increase at higher polymer concentrations. A similar behavior of the high-shear viscosity was reported by Rossi et al. (2003) for bentonite dispersions with non-ionic polymers.

Addition of a low-viscosity CMC to a 6% dispersion of an unspecified type of bentonite did not affect the small yield stress of the dispersion (Dolz et al., 2007). Benchabane and Bekkour (2006) reported that addition of CMC to a 5% calcium bentonite–CMC dispersion resulted in a behavior more likely to the pure CMC solution than the pure bentonite dispersion. However, their Fig. 2 showed that for shear rates  $>1$  s<sup>-1</sup> the bentonite–CMC dispersions were very similar to the pure bentonite dispersions. XRD measurements revealed that CMC was only adsorbed on the external surfaces preventing further particle interaction, which may explain the plateau value of the yield stress reported in our work. Benyounes et al. (2007) reported also that the behavior of 3% bentonite dispersions containing small amounts of CMC was similar to pure CMC solutions. Closer inspection of their data, however, showed that even the pure 3% bentonite dispersion did not exhibit a true Herschel–Bulkley behavior showing no definite yield stress, which was more evident at  $>4%$  bentonite contents. Kok and Iscan (2009) reported an increase of

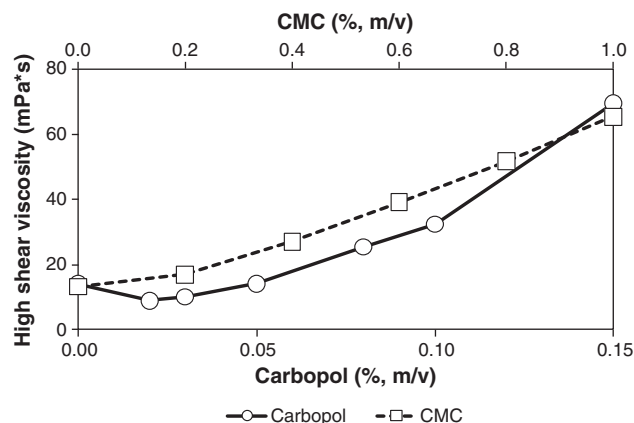


Fig. 11. High shear viscosity (at  $1021 \text{ s}^{-1}$ ) of 3% bentonite–CMC and 3% bentonite–Carbopol dispersions.

the yield stress of 6.42% bentonite–CMC dispersion after the addition of 1, 2, 3, and 4%. The data were well described by the Herschel–Bulkley model. Zhang et al. (2000) reported increase in apparent viscosity, plastic viscosity and yield point after the addition of 0.2% CMC to the 4% dispersions of unspecified bentonite using only two measurement points. Singh and Sharma (1991), who also used only two-point measurements, reported an initial decrease of the yield point followed by an increase. Singh et al. (1992) on the other hand reported increased shear stress values measured at all shear rates for bentonite–CMC dispersions at all studied temperatures, however they did not report the amount of CMC they used.

It is apparent then that a direct comparison of our results with the scarce prior data on the effect of CMC addition on the rheological behavior of bentonite dispersions cannot really be made. The main reason is that a different, sometimes unspecified, bentonite was used, despite the fact that the bentonite type is very important for the rheological behavior and the way the particles interact with the polymers. Furthermore, in all prior work many investigators used two point measurements which are routinely used in oil-field drilling but do not allow for full assessment of the rheological behavior of the dispersions.

## 7. Conclusions

The effect of addition of CMC and Carbopol on the rheological properties of sodium-bentonite dispersions was investigated. The rheological behavior of the pure CMC solutions could be described by the power law model. The viscosity of the dispersions increased with the concentration of the polymer. The Carbopol solutions showed Herschel–Bulkley behavior with the yield stress and the flow consistency index increasing in a power law fashion with increasing polymer concentration while the flow behavior index decreased at first and then remained fairly constant.

The influence of CMC on the rheological behavior of 3% bentonite dispersions and of Carbopol on 3 and 4% bentonite dispersions was investigated. The appropriate rheological model was the Herschel–Bulkley model with all formulations showing pseudoplastic behavior with a yield stress. For the bentonite–CMC dispersions both the yield stress and the flow consistency index decreased, then increased with polymer concentration. The yield stress reached a plateau, indicating that at higher polymer concentration the viscosity increased due to the increased viscosity of the CMC solution. The minimum was attributed to the liquefying effect of the CMC. The adsorption studies showed that CMC was adsorbed onto the bentonite particles via a Langmuir isotherm of L1 type indicating monolayer surface coverage.

The yield stress and the flow consistency index of the bentonite–Carbopol dispersions also showed a minimum with increasing polymer

concentration. Both parameters showed a power law increase at higher polymer concentrations, similar to the pure Carbopol solutions. Adsorption of Carbopol onto bentonite particles also followed the Langmuir isotherm of the L1 type.

The adsorbed amounts of Carbopol and CMC differed by an order of magnitude. Related to the carboxyl group contents the adsorbed amounts were of similar order of magnitude i.e. 2.1 and 0.6 mmol COOH per gram bentonite for CMC and Carbopol. Similarly, the minimum of the yield stress of the bentonite polymer dispersions corresponded to 0.28 mmol and 0.16 mmol for CMC and Carbopol.

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