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ADSORPTION BEHAVIOR OF CATIONIC POLYMERS ON BENTONITE

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The adsorption behavior of a series of cationic water-soluble polymers poly(diallyldimethylammonium chloride) with different molar masses onto raw bentonite was investigated through the elaboration of their adsorption isotherms and the quantification of the water content of the clay/polymer complexes formed. It was found that the type of adsorption isotherms obtained depends on the chain length of the polymer. The study showed a correlation between the amount of adsorbed polymer and the water content of the clay, after the adsorption experiments. The lower the molar mass of the polymer used, the larger was the reduction on water content of the complexes.

Keywords: *bentonite, cationic polymers, drilling fluid, thermogravimetry*

Introduction

The study of polymer adsorption on solid/liquid interfaces based on clay-polymer interactions has found a wide range of practical applications in very important technological fields including the stabilization of colloidal dispersions and soil particles surface modification [1, 2]. In oil well drilling operations, for example, different types of polymers are added to the drilling fluids for controlling the smectite rich shale reactivity, suppressing clay dispersion and swelling. Problems, such as instability of wellbore that can slow down the drilling process and increase enormously the cost of operation. The drilling fluids stabilizing action depends on the clay/polymer interaction, although the mechanism of such interaction is not well understood. An estimate of USD 500 million is lost every year worldwide directly or indirectly caused by wellbore instability [3, 4].

Cationic polymers such as poly(diallyldimethylammonium chloride) PDADMAC, are widely used in water based drilling fluids formulations in the concentration range from 0.1 to 5 mass/mass% in order to provide shale inhibition properties and minimize the dispersion of the drilled cuttings [5]. Polycations are known to adsorb readily onto smectite rich clay minerals from aqueous solutions [6–9] and the presence of considerable quantities of polymer in the interlamellar space prevents the water uptake by the clay avoiding swelling and dispersion. Water molecules on clay minerals surfaces are associated with the clays exchangeable cations and temperatures above 100°C are necessary in order to release them [10–12]. In addition, these water molecules compete with the polymers for adsorption sites on the clay surface. Although it is well known that the water content plays an important role on the clay reactivity, there are few studies reporting the influence of the water associated with the clay surface on the polymer adsorption [13].

The aim of this work was to characterize the complexes obtained through the adsorption of cationic polymers (PDADMAC) on natural bentonite by means of their adsorption isotherms, the bound water content and the basal spacing of the clay/polymer systems. The influence of the polymer chain length on these parameters was investigated by elemental analysis of C, H and N, thermogravimetric analysis and X-ray diffraction. A methodology based on the thermogravimetric analysis was employed in order to correlate the clay/water content of the complexes with the adsorbed polymer amount since this information may be very important for understanding and controlling the wellbore stability.

Experimental

Materials

The cationic polymers used in this study were the poly(diallyldimethylammonium chloride) with high (500000–400000), medium (350000–200000), low (200000–100000) and very low (100000–20000) molar mass. The PDADMAC contains a pyrrolidinium ring with a quaternary ammonium group which possesses a formal positive charge at all normal pH values. The distance between the charged centers calculated by molecular models of adsorption is of 74 nm as previously reported [14]. All polymers were characterized by $^{13}C\{^1H\}$ NMR obtained on a

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Brucker Advance DPX-200 spectrometer at 75.5 MHz. Polymer NMR spectra were performed in D_2O solutions and the reported chemical shifts are relative to tetramethylsilane (primary reference) and to 1,4-dioxane as a secondary reference at 67.40 ppm. No residual monomers could be detected in the spectra as indicated by the absence of the typical signals of allylic moieties. The polymers were supplied by Sigma-Aldrich Company and were used without any further purification.

Bentonite supplied by Bentonorte Company (Paraiba, Brazil) was used in the adsorption experiments. The bentonite was used in its native exchanged form, i.e., a mixture of Na^+ and Ca^{2+} forms. X-ray diffraction analysis of the bentonite showed that it contains 50% of smectite, 22% of kaolinite and also impurities, mainly quartz (20%) and calcite (5%). The characteristics of the bentonite such as its cation capacity exchange (CEC) surface area and mean particle size are shown in Table 1. The relatively low values of CEC and surface area may be attributed to the impurities present in the clay.

Methods

Adsorption experiments

The adsorption studies were performed by means of a batch technique to obtain equilibrium data. Samples were prepared by adding of 5.0 g of bentonite to a polymer solution of known concentration and this solid to liquid ratio was kept constant for all experiments, as well as the pH of the polymer solutions. The clay/polymer suspensions were shaken in a water bath at 32°C for 2 h. Afterwards, the suspensions were centrifuged at 5.000 rpm to settle the solids. Then, the samples were oven-dried at 100°C grounded and stored in sealed flasks in order to keep them far from external humidity. All samples were prepared in duplicate, in order to obtain a mean value of the adsorption and water loss measurements. The amount of polymer adsorbed on the clays was determined by elemental analysis of C, H and N using a FlashEA-1112 ThermoFinnigan apparatus. The blank (control test) was run submitting the clay to the same conditions of the adsorption experiments, however without the addition of polymer.

Thermogravimetric analysis

The water content of the clay/polymer systems was determined by thermogravimetric analysis in a Shimadzu TGA-51 apparatus using a methodology developed by Santos [15]. Samples with defined mass were heated from 30 to 200°C at a heating rate of 10°C min^{-1} under dry N_2 atmosphere as carrier gas. All samples submitted to TG analysis were previously sieved on a 200 mesh screen. The samples were dried under nitrogen flow for 10 min prior to initiating the heating ramp to remove the physisorbed water. Keeping the sample preparation and the method constant, variation in the water content can be compared for different samples as described elsewhere [16].

XRD analysis

X-ray diffraction analysis for pressed powder samples were obtained using CuK_α radiation (λ=1.5418 Å) on a Siemens/Brucker – AXS D5005 diffractometer operating at 45 kV and 35 mA at 2θ scan rate of 0.005 Å min^{-1}.

Results and discussion

Adsorption isotherm

In Fig. 1 the uptake curves for the cationic polymers with different molar masses (HMW, MMW, LMW, VLMW) on bentonite are presented. The adsorption profiles of PDADMAC-VLMW on bentonite showed the characteristic shape of an L type isotherm. They

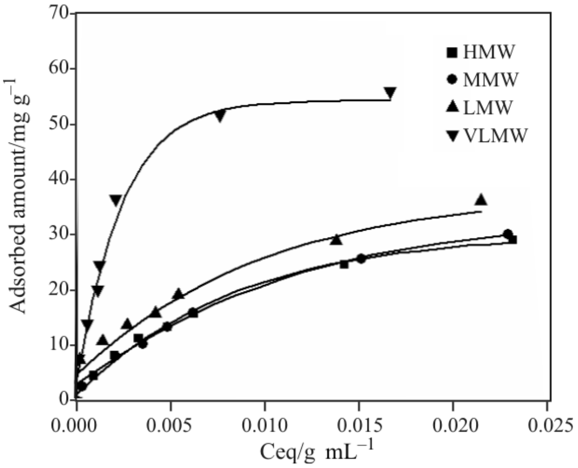

Fig. 1 Adsorption isotherms of PDADMAC-HMW, MMW, LMW, VLMW on bentonite

Table 1 Bentonite characteristics

Exchangeable cations[a]	Cation exchange capacity[b]	Surface area[c]	Mean particle size[d]
Na^+, Ca^{2+}	65 meq/100 g	48.53 m^2 g^{-1}	1.2 μm

[a]from XRF analysis, [b]from methyleneblue method, [c]from BET method, [d]by Malvern Mastersizer analyzer

Table 2 Langmuir data for PDADMAC adsorption onto bentonite

Polymer	N_m/mg g^{-1}	R/95%
PDADMAC-VLMW	62.5	0.9975
PDADMAC-LMW	41.1	0.9659
PDADMAC-MMW	40.3	0.9783
PDADMAC-HMW	38.7	0.9949

show an initial strong increase of the adsorbed amount with the increase of polymer concentration in the solution, followed by a pseudo-plateau which corresponds to the saturation of the surface by the polymer chains [17]. However, for the other polymers the plateau region was not observed and the adsorbed amount of polymer increased continuously over the whole concentration range. Thus, the adsorption isotherms showed the influence of the polymer chain length on the adsorption process suggest strongly that polymers with lower molar mass may have more access to the interlayer spaces of the smectite-rich clay systems.

In order to quantify the adsorbed amount of polymers all adsorption data were analyzed according to the linearized Langmuir Eq. (1). The mass of polymer per gram of clay needed to form a monolayer (N_m) was obtained by plotting the equilibrium concentration (C_e) *vs.* C_e/N, where N is the mass of polymer per gram of clay at some equilibrium concentration yielding a straight line with slope $1/N_m$.

$$\frac{C_e}{N}=\frac{C_e}{N_m}+\frac{1}{KN_m} \qquad (1)$$

The adsorbed amount of polymer needed to form a monolayer (N_m) onto bentonite and the respective correlation coefficients are shown in Table 2. The N_m values decreased with increasing molar mass as expected for the adsorption of polymers on porous adsorbents like clays and are in reasonable agreement with those obtained previously [6, 9]. It is important to note that in spite of using a heterogeneous bentonite to simulate the wellbore conditions the observed adsorption behavior was determined by the fraction of smectite in the clay. The low correlation coefficient for Langmuir linearization may be attributed to the heterogeneity of the raw bentonite. Even though, these results clearly show that cationic polymer adsorption onto smectite-rich clay is strongly influenced by the polymer chain length as previously reported in [18].

Typical TG/DTG pattern can be observed for cationic polymers/bentonite complexes in Fig. 2 for a PDADMAC-HMW loading. A similar trend was observed for the other polymers. The first mass loss region between 30–200°C was due to the release of water adsorbed on the surface of the clay particles (i.e., bound water), predominantly from the interlayer spaces of smectite [19–21]. The following mass losses derived from thermal decomposition of polymer and from the dehydroxylation of clay minerals.

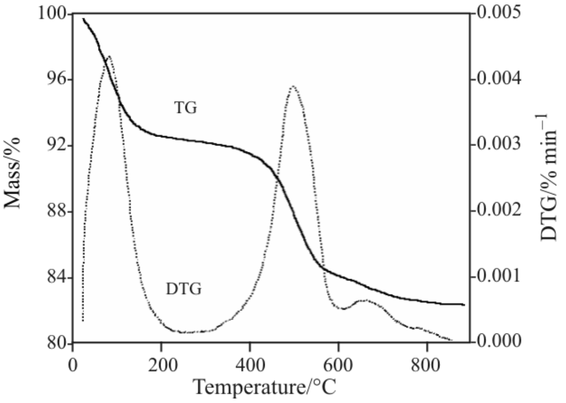

Fig. 2 TG/DTG curves of PDADMAC-HMW/bentonite complex in the polymer concentration of 0.2 mass/mass%

According to the results shown in Fig. 3 increasing the polymer loading implies changes on the thermal stability of the clay/polymer complexes, mainly in the first thermal event, when the desorption of bound water occurs. These data are in agreement with the idea that the polymer chains compete with the water molecules for the adsorption sites on the clay, since the intensity of the first peak decreases as the polymer concentration increases. Thus, using the methodology developed by Santos [15] to measure the bound water content of clay minerals it was possible to follow up the decrease of the first peak (percentage of mass loss of clay/polymer complexes) as the polymer loading is increased in a concentration range from 0.2 to 3.0 mass/mass%.

All studied polymers were able to decrease the amount of bound water adsorbed on clay. Figure 4

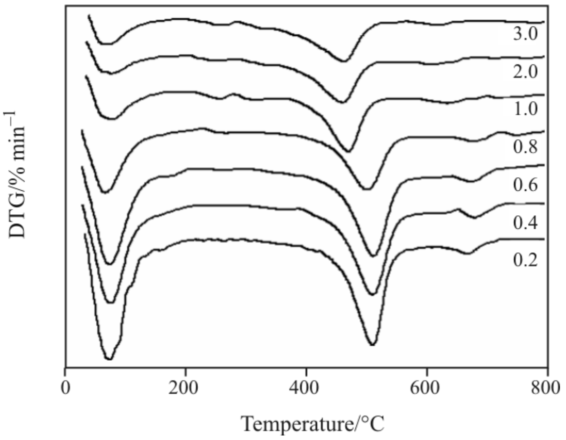

Fig. 3 DTG curves of PDADMAC-HMW/bentonite complexes in the polymer concentration range from 0.2 to 3.0 mass/mass%

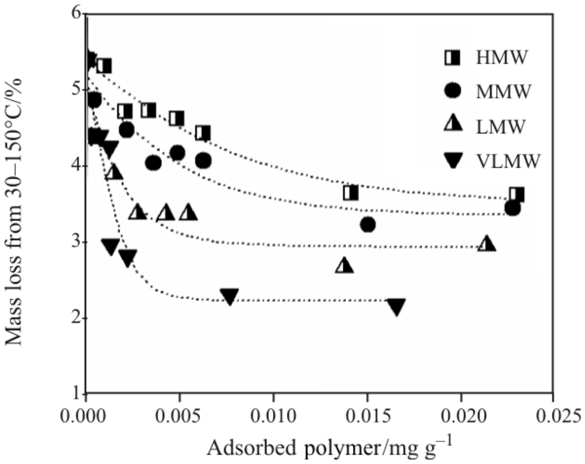

Fig. 4 Correlation of mass loss data from TG with the adsorbed amount of polymers from adsorption isotherms for all cationic polymers

compares the amount of cationic polymer adsorbed on bentonite from adsorption isotherms with the mass loss in percentage from 30 to 200°C in the TG/DTG experiments. These results show that the cationic polymer adsorption on bentonite is directly related to the water content of the clay/polymer complexes. In this way, as the adsorbed amount of polymer increases with the increase in the polymer loading, the water content of the complexes is reduced according to the molar mass of the polymer. The highest reduction observed in the temperature range from 30 to 200°C was for complexes with PDADMAC-VLMW and these values decreased until a plateau region was reached at 2.5%. On the other hand, the values obtained for the higher molar mass polymers decreased continuously and no plateau region was observed. This behavior is in agreement with the adsorption data and confirms the supposition that the adsorption process of cationic polymers on bentonite is favorable for smaller polymers, which may have an easier access to the interlayer spaces of the clay than for bulky polymers. This information is very important for the development of cationic additives for drilling fluids, since wellbore instabilities are directly related to the water interaction with the shale. Thus, shorter cationic polymer chain length seems to be more efficient for that purpose promoting a better adsorption of the polymer and reducing the bound water adsorbed on clay.

In spite of all evidences that polymers with lower molar mass may penetrate to the interlayer spaces of the clay, this hypothesis may only be supported by X-ray diffraction techniques. The diffractograms of the clay/polymer complexes are shown in Fig. 5 as well as the one from raw bentonite submitted to the same adsorption conditions (blank).

All clay systems exhibited a basal spacing of ca. 15.5 Å after the adsorption experiments. Although it is well documented that this d_{001} value may correspond to one layer of PDADMAC occupying the interllamellar spaces of smectite clay [22, 23] those results should be interpreted with care since the present authors are dealing with a heterogeneous clay. Pure bentonite showed two very broad peaks at 12.6 and 15.5 Å which may be associated to the hydrated cations, Na^+ and Ca^{2+} between the aluminosilicate layers. The adsorption of very low molar mass cationic polymer on bentonite yielded a sharper peak at 15.5 Å suggesting that an ordered structure was obtained compared to the other polymers. Nevertheless, this is not sufficient to assure that PDADMAC-VLMW has penetrated the basal spaces of clay.

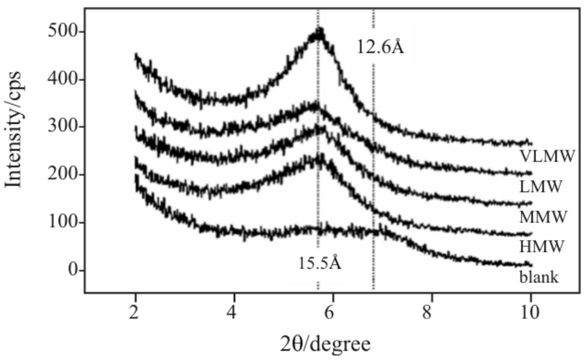

Fig. 5 XRD patterns of PDADMAC-HMW, MMW, LMW, VLMW/bentonite complexes in the polymer concentration of 3.0 mass/mass% and blank

Conclusions

The effect of polymer chain length on the adsorption of cationic polymers onto bentonite was evaluated by means of their adsorption isotherms and their thermal stability. Cationic polymers with lower molar mass showed more affinity for adsorption on clay than higher molar mass polymers, also promoting greater reduction on the clay/water content. The methodology adopted to measure the amount of bound water in the clay/polymer complexes showed to be a good approach to correlate the adsorption data with the quantity of water that remains adsorbed on clay.

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