Hydrophobically Modified Poly(ethylene glycol) as Reactive Clays Inhibitor Additive in Water-Based Drilling Fluids

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ABSTRACT: Adsorption measurements and inhibition tests were used to investigate the mechanisms of shale stabilization by hydrophobically modified poly(ethylene glycol) (PEG). Commercially available PEG with a large range of molar masses and PEG diesters were adsorbed on smectite-rich clay from saline solutions and the clay/polymer complexes obtained were characterized by thermogravimetric analysis and x-ray diffraction. The adsorption isotherms obtained for all unmodified PEG showed low affinity for the clay surface, however they all accessed the interlamellar spaces of the clay and reduced the clay water content of the complexes obtained. The PEG macromolecules had their affinity for the clay strongly enhanced by the hydrophobic modification especially with dodecanoic acid and were intercalated into the clay matrix, reducing, in a more efficient way, the water uptake by the clay. Conventional rolling tests were performed to evaluate the effect of polymers on the clay cuttings integrity. Results show that under conditions promoting the adsorption of polymers on both external and interlayer clay surfaces, displacement of the water from the clay was obtained and dispersion and disintegration of clay cuttings were inhibited. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 857–864, 2010

Key words: adsorption; poly(ethylene glycol); clay; structure-property relations; water based drilling fluid

INTRODUCTION

The adsorption of polymer molecules at solid/liquid interfaces is at the basis of many technological applications,[1] such as enhanced oil recovery, mineral beneficiation, coatings, waste treatment and, specially, as shale inhibition additive in water based drilling fluids (WBDF).[2–8] One of the main important functions of the drilling fluid is to prevent the degradation of the wellbore walls and the disintegration and dispersion of drilled cuttings into the fluid.[9] Reactive shales are found in 75% of the formations drilled all over the world and are responsible for 90% of the wellbore instability problems.[10] These heterogeneous shales, containing smectite-rich clay minerals and other several minerals, may swell and disintegrate in contact with water, leading to serious borehole problems. Clay/polymer interactions have shown to play an important role during the drilling of oil wells when WBDF are used.

Glycol, poly(ethylene glycol) (PEG) and poly(alkylene glycol) derivative additives also called polyols have been used as inhibitive WBDF and are usually employed in conjunction with KCl to reduce clay swelling and to produce firmer cuttings which can arrive to the surface with minimum dispersion and disintegration.[11–13] Moreover, increased drilling rates and reduced environmental impact of drilling operations are also reached with these systems.[14–16]

Although there is still a controversy about the inhibition mechanisms of polyol additives, it is usually considered that there is a competition between polyol and water molecules for the adsorption sites on the clay minerals present in the shales. The adsorption seems to be based on ion-dipole interactions between the exchangeable cations of smectite and the polyols polar functional groups. Besides, H-bonding, van der Waals interactions and entropy effects can contribute significantly to the adsorption of PEGs on the clay surfaces.[17-24] On the other hand, for hydrophobically modified PEGs the adsorption behavior is quite different from that observed for homopolymers and is influenced by the balance of hydrophilic moieties (ethylene oxide units) and the lipophilic moieties (aliphatic groups).[25–28] Both unmodified and the hydrophobically modified PEG's, are able to readily penetrate the interlamellar

TABLE I
Cation Exchange and Surface Properties of Clays

Clay	Exchangeable cations[a]	CEC[b]	SA[c]	MPS[d]
Bent1	Na^+, Ca^{2+}	68 meq/100 g	112 m^2/g	4.9 μm
Bent2	Na^+, Ca^{2+}	140 meq/100 g	253 m^2/g	2.0 μm

[a] From XRF analysis.
[b] From methyleneblue method.
[c] From BET method.
[d] By Malvern Mastersizer analyzer.

spaces of smectite-rich clays. The hydrophobically modified prevent the water uptake by the clay and hence their swelling and dispersion in aqueous medium. Although it is well known that the polymer adsorption plays an important role on the shale inhibition, there are few studies reporting the influence of the structure of the polymers on the maintenance of the clay cuttings integrity or even the stability of the wellbore.[29-31]

This work aims to contribute to a better understanding of the adsorption and inhibition process of PEG and hydrophobically modified PEG onto a smectite-rich clay. PEGs with a large range of molar masses were studied to elucidate their ability to penetrate into the clay matrix and decrease the water uptake by the clay, respectively by x-ray diffraction and thermogravimetric analysis of the obtained systems. The dependence of the adsorbed amount on polymer concentration and on the molar mass of the polymer is discussed. Hydrophobyzed PEGs with acetic acid and lauric acid have been studied to investigate the influence of hydrophobic segments in the adsorption process and inhibition properties. Finally, the effect of these polymers and KCl solutions on the integrity the of clay cuttings is qualitatively related to the adsorption characteristics.

EXPERIMENTAL

Materials

Ethylene glycol polymers with different molar masses (400, 1500, 4000, 6000 g/mol) were used in this study as adsorbates. The polymers were supplied by VETEC S.A. (Rio de Janeiro, Brazil) and were used without any further purification. The diesters of PEG400 were synthesized and characterized by FTIR spectroscopy (Nicolet 740FTIR) and by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Brucker Avance DPX-200 at 75.5 MHz).

The clays used in the cuttings rolling tests and adsorption experiments were two bentonites (Bent1 and Bent2) supplied by Bentonorte Company (Paraiba, Brazil). The Bent1 is a natural clay mineral containing smectite (50%), kaolinite (22%) and also impurities, mainly quartz (20%) and calcite (5%).

The Bent1 was sieved to yield 23.6–4.76 mm size granules, as recommended for the cuttings rolling test[32] and stored in sealed flasks. The Bent2 is manufactured from bentonite rocks by removing impurities and by treating with sodium carbonate solutions. The XRD analysis of Bent2 showed that it consists mainly of irregular interstratifications of illite/smectite (94%) and kaolinite (4%) and also some impurities such as quartz (1%). The characteristics of the Bent2, such as cation exchange capacity (CEC), surface area (SA) and mean particle size are shown in Table I.

Adsorption experiments

The adsorption experiments were performed by means of a batch technique to obtain the equilibrium data. Samples were prepared by adding 1.25 g of bentonite to a polymer saline solution of known concentration (in the range from 0.05 to 0.2 g/mL) and the solid to liquid ratio was kept constant for all experiments, as well as the pH of the polymer solutions, which was kept at 5–6. The clay/polymer suspensions were shaken in a water bath at 32°C for over 16 h. Afterwards, the suspensions were centrifuged at 5.000 rpm to settle the solids. The samples were oven-dried at 90°C, ground and stored in sealed flasks to preserve them from external humidity. All samples were prepared in duplicate to obtain a mean value of the polymer adsorption by Carbon, Hydrogen, and Nitrogen elemental analysis (CHN analysis) and water loss measurements (by TGA/DTG analysis). The amount of polymer adsorbed on the clays was determined by CHN analysis using a FlashEA-1112 ThermoFinnigan apparatus. A blank (control test) was run submitting the clay to the same conditions of the adsorption experiments, however without the addition of polymer.

TGA/DTG analysis

The water content of the clay/polymer systems was determined by thermogravimetric analysis, in a Shimatzu TGA-51 apparatus, using a methodology developed by Santos.[33] Samples with defined mass were heated from 30 to 800°C with a heating rate of

10°C/min under dry N_2 atmosphere as carrier gas. All samples submitted to the TGA analysis were previously sieved on a 200 mesh screen. The samples were dried under nitrogen flow for 3 min before initiating the heating ramp to remove the physisorbed water. So, keeping the sample preparation and the drying method constant, variations on the water content from different samples could be compared.

XRD analysis

The X-ray diffraction analysis for pressed powder samples were obtained using CuKα 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}.

Cuttings rolling tests

The cuttings rolling tests were performed following the procedure of Beihoffer,[32] slightly modified. This test quantitatively estimates the extend of intergranular cohesion and the resistance to hydration forces and mechanical stresses within the shale cuttings, after contact with the drilling fluid. Fifty grams of sized clay (Bent1) were rolled for 16 h at 66°C in 350 mL (one laboratory barrel) of the test fluid in a stainless steel aging jar. After rolling, the clay was collected on a 0.12 mm sieve—called dispersed material—and then washed with distilled water. The clay was then collected on a 4.76 mm sieve, to evaluate the material percentage that maintained the original size—called intact material. The cuttings were then dried to a constant weight in an oven at 100°C. The percent recovery of Bent1, after correcting the original mass for the water content of the clay (10%), was calculated on a dry mass basis as follows: % $R = W/W_o \times 100$, where W and W_o denote the weight after and before rolling, respectively. Clearly, the more inhibitive the fluid, the lower the level of cuttings dispersion and hence the higher the final recovery.

RESULTS AND DISCUSSION

Adsorption

The samples of PEG with different molar masses exhibited low affinity for the bentonite as indicated by the initial slope of the adsorption isotherms in Figure 1. Increasing the molar mass of the PEG from 400 to 1500, increased the adsorbed amount of polymer. However, when increasing the mass from 4000 to 6000, a slight decrease in the adsorption was observed, mainly at higher polymer concentrations. This behavior was also reported by Zhao,[19] who
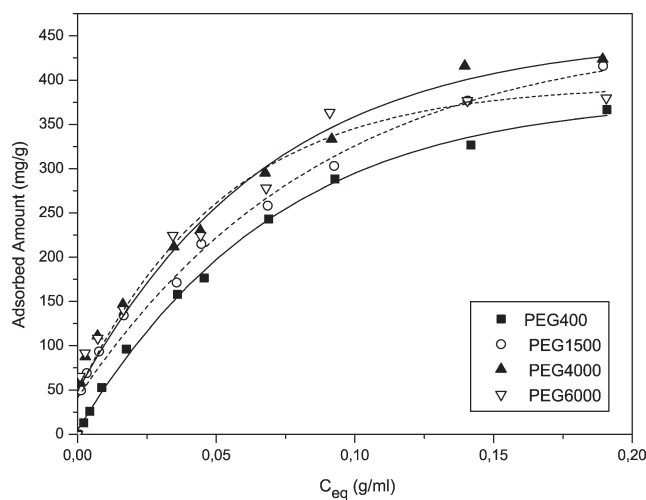
Figure 1 Adsorption Isotherms of PEGs onto bentonite Labels. X, equilibrium concentration, Ceq (g/mL) Y, adsorbed amount (mg/g). Full symbol, straight line; empty symbol, dash line.

showed that PEG polarity weakens and its affinity to water decreases with increasing the molar mass of the polymer, favoring the adsorption process. Parfitt[20,21] observed changes in the isotherm shape of PEG adsorption on clay, with different molar masses, attributing these modifications to the changes in conformation of the PEG molecules in solution from linear to random coil. Therefore, as the molar mass increases, the polarity of the macromolecular chain weakens, leading the polymer to adopt a more random coil conformation in solution and, thus, adsorbing at clay surface preferentially with segments in loops and tails. This may induce a contraction of the active SA by bridging between two consecutive clay platelets, reducing the accessibility of the adsorbing sites on the clay and so decreasing the adsorbed polymer amount.

The adsorption data of the PEGs were fitted according to the Langmuir equation, Ceq/N = Ceq/Nm + 1/KNm, where the mass of polymer per gram needed to form a monolayer (Nm) was obtained by plotting the equilibrium concentration (Ceq) versus Ceq/N, yielding a straight line with slope 1/Nm. The maximum adsorbed amounts Q_{max} (mg of polymer/g of clay) of PEGs with different molar masses and the respectively correlation coefficient (R) are shown in Table II.

The Q_{max} of PEG initially increases from PEG400 to PEG1500 but then it decreases from PEG4000 to PEG6000. These values were greater than the ones reported by other authors for nonionic polymer adsorption on clay.[19–24] Rossi[22] reported a Q_{max} value for PEG1500 of 140 mg/g and Zhao[19] reported that the maximum amount of PEG2000 adsorbed onto Na-montmorillonite was 100 mg/g. This may mean that the clay employed in this work may be

TABLE II
**Adsorption Parameters for the Adsorption of
PEGs on Bentonite**

PEG	Q_{max} (mg/g)	K_d	R (99%)
400	524	12.16	0.9992
1500	535	15.75	0.9823
4000	516	22.22	0.9779
6000	448	30.67	0.9715

more reactive. It is not uncommon find different Qmax for the same clay/polymer systems and even differences in the way the workers brought the reactants together might significantly influence adsorption results.[17] Breen[34] found that the use of the fine fractions of clay, obtained by sedimentation, exerted great influence on both the affinity and the amount of polymers adsorbed.

As observed on Table II, the Langmuir constant K_d increases continuously. The parameter K_d represents the affinity of the polymer for the clay surface. Thus, increasing the polymer chain length will enhance the number of interaction points between the PEG chains and the clay surface, increasing the adsorbed amount of polymer. These interactions may include van der Waals forces, hydrogen bonding and ion-dipole interactions between the clay surface and the ethoxy group (or the terminal hydroxyl groups) of the PEG, however this process is not fully understood.[19–22]

The adsorption process of PEG was significantly changed when hydrophobic segment was incorporated at the end of the macromolecule, as shown in Figure 2. Despite the fact that PEG400-C_2 has no terminal hydroxyls to be anchored by hydrogen bonding to the clay surface, it showed the same affinity
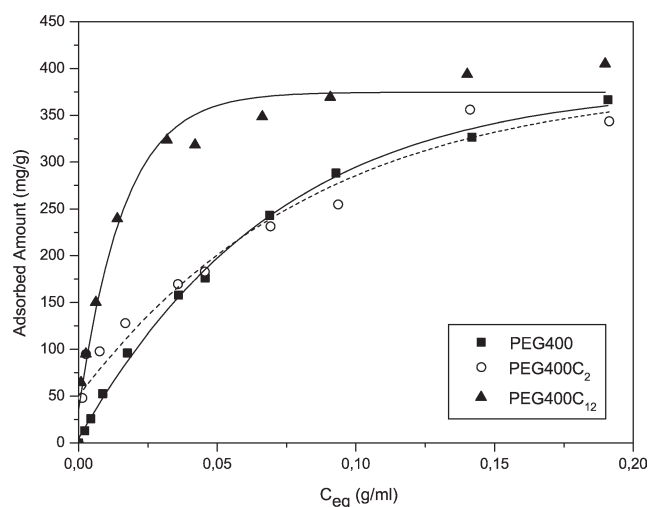
for the bentonite as do PEG400. This is in agreement with the idea that PEG adsorption on clay is based on the interactions between the ethylene oxide segments (OCH_2CH_2) and the silanols from the silica surface. On the other hand, the PEG400-C_{12} exhibited a greater affinity for the bentonite surface than the PEG400 and the PEG400-C_2. The adsorbed amount of PEG400-C_{12} increased with polymer loading, reaching a pseudo-plateau at polymer concentration of about 0.10 g/mL, which corresponds to the saturation of the surface by the polymer chains.

The maximum adsorbed amount (Q_{max}) for the two types of hydrophobically modified PEG, which corresponds to the polymer monolayer formation, was almost the same (Table III). However, the adsorption process of PEG400C_{12} was clearly favored, as compared with the one for PEG400C_2 (Fig. 2). The K_d values, shown on Table III, confirm that the dilaurate of PEG400 has more affinity for the clay surface than the diacetate. This behavior may be attributed to additional interactions between the lauric chains (hydrophobic interactions) and chain entanglements, leading to greater amounts of polymer adsorbed on the clay surface. Volpert[28] reported that hydrophobic modification of polyacrylamide enhanced considerably its affinity for silicate surface due to the possibility of chain reorganization in the adsorbed layer and to a successive formation of additional polymer layers by hydrophobic association.

Water uptake

Thermal analysis results for all clay/polymer complexes in the temperature range of 30–800°C show three distinct weight loss steps corresponding to different thermal events. We have focused on the first thermal event, between 30 and 120°C, associated with the loss of adsorbed water from external surface and on the interlayer of the smectite-rich clay (hydration water). The other events were associated to losses of polymer degradation products (between 200 and 420°C) and of the clays structural hydroxyl groups (between 450 and 550°C). Figure 3 presents the weight loss results from the region between 30 and 120°C, corresponding to a dehydration event for the clay/PEG systems with different polymer molar

Figure 2 Adsorption Isotherms of hydrophobically modified PEGs onto bentonite Labels. X, equilibrium concentration, Ceq (g/mL) Y, adsorbed amount (mg/g). Full symbol, straight line; empty symbol, dash line.

TABLE III
**Adsorption Parameters for the Adsorption of
Hydrophobically Modified PEGs on Bentonite**

PEG	Q_{max} (mg/g)	K_d	R (99%)
400	524	12.16	0.9992
400C_2	419	21.78	0.9644
400C_{12}	413	100.15	0.9958
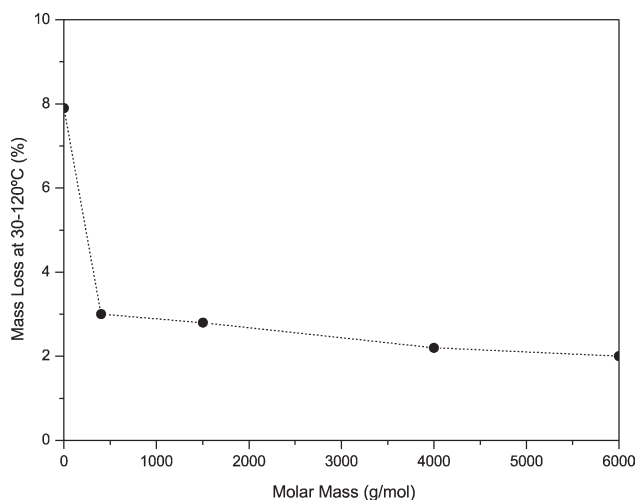
Figure 3 Weight loss in the range of 30–120°C of clay/PEGs with different molar mass adsorption onto bentonite. X, molar mass (g/mol) Y, mass loss at 30–120°C (%).

masses, at the highest polymer concentration studied (i.e. 20.0 wt %). As previously reported,[35,36] the PEGs are able to reduce the hydration water of the clay/polymer complexes. It was observed a significant decrease in the water content when using PEG400. However, for higher molar mass polymers, these values remained constant as the plateau was reached. Since the remaining water of the clay/polymer complexes may be attributed mainly to the water adsorbed on the interlayer of the smectite-rich clay, it can be suggested that all PEGs have similar access to the clays adsorption sites.

As shown in Figure 4, both modified PEG400 were able to drastically reduce the water content of the clay/polymer complexes, as compared to the
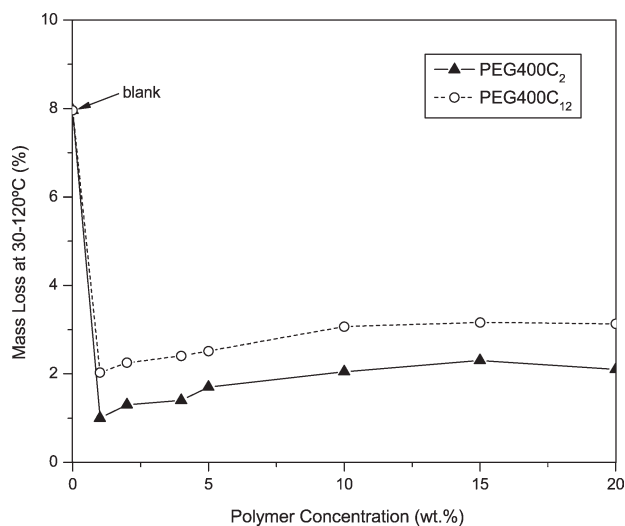
Figure 4 Weight loss in the range of 30–120°C of hydrophobically modified PEGs adsorption onto bentonite. X, polymer concentration (wt %) Y, mass loss at 30–120°C (%). Full symbol, straight line; empty symbol, dash line.

water content of the pristine clay sample (blank). The values obtained with the $PEG400\text{-}C_{12}$ were lower than those obtained with $PEG400\text{-}C_2$, which agrees with the adsorption isotherm data. Since the adsorption process is enhanced by the estherification of the adsorbates, the water content of the clay/polymer complex is reduced proportionally to the increase in the size of the hydrophobic segments.

However, as the polymer load increases, the weight loss associated to the remaining water in the clay/polymer complexes have also shown a slight increase. The same behavior was observed by Montarges et al.[37] for the adsorption of poly(ethylene oxide)/poly(propylene oxide) copolymers onto montmorillonite, suggesting that, for higher polymer concentrations, these polymers may be located both in the interlayer space and on the external surfaces of the clay.

Clay/polymer structure

The d_{001} spacings of clay, treated with water, potassium chloride solution (3 wt %) and 20.0 wt % aqueous solutions of PEGs (with and without KCl), are listed in Table IV. The results show that PEG of different molar mass are able to intercalate into the interlamellar spaces of the clay, exhibiting a molar mass effect in agreeing with previously reported results.[21-24] Increasing the molar mass (from 400 to 6,000 g/mol) resulted in further expansion of the clay interlayers (from 14.7 to 22.7 Å) to accommodate the increasing mass of PEG. On the other hand, when the bentonite was treated with polymeric saline solutions, the observed values of basal spacing were almost invariable (about 14.3 Å). This results may be attributed to the residence of only one polymer layer in the basal spacings of the clay.[18] It is known that potassium ions are reluctant to form a full hydration shell, preferentially binding clay surfaces and bringing them close together. This effect reduces the tendency of K^+ saturated smectites to expand, even with high polymer loadings, as previously reported.[7] This effect is also evident when

TABLE IV
**First-Order Basal Spacings of Clay/PEGs Complexes**

Sample	d_{001} (Å)	
	Non saline medium	Saline medium (3 wt % KCl)
H_2O	14.1	12.5
PEG400	14.7	14.2
PEG1500	15.5	14.4
PEG4000	18.0	14.3
PEG6000	22.7	14.3
$PEG400C_2$	17.1	14.0
$PEG400C_{12}$	17.2	13.9

comparing the values of d_{001} for control experiments, with the results with de-ionized water and potassium chloride solution, which showed, respectively, the clay with a double layer of water (14.1 Å) and the more dehydrated clay, with a interlamellar spacing of 12.5 Å (attributed to one layer of water).

The same trend was observed for the clay treated with modified PEGs in saline solutions exhibiting a constant value of about 14.0 Å, which may be assigned as one layer of polymer in the interlamellar spaces of the clay. On the other hand, in non saline medium, both diesteres of PEG showed d_{001} value of about17.0 Å, which is characteristic of the formation of bilayer complexes.[26,27] These results suggest that the PEG chains adsorb on the interlayer spaces of the clay, while the alkyl segment is kept on the external surfaces. This adsorption model is particularly interesting for the PEG inhibition mechanism, since it predicts that the hydrophobic alkyl chains of modified PEGs could block the interlayers of the clay, hindering the water entrance thus, preventing swelling and disintegration of clay particles. The cuttings rolling tests support this model, showing that the clay in contact with lauric acid modified PEG exhibit an excellent recovery of intact clay cuttings, as discussed next.

Inhibition properties

The effect of the saline medium on the inhibition properties of PEG400 is shown in Figure 5. The results clearly show the synergy observed when the polymer and KCl are used together, as previously reported.[13] Therefore, the other experiments with unmodified and modified polymers were performed in saline media of 3 wt % KCl.
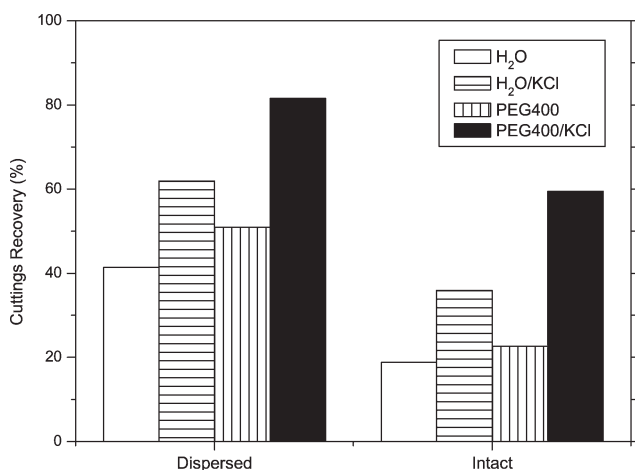
Figure 5 Cuttings recovery percentage obtained with 20 wt % PEG400 with and without addition of KCl Labels. X, dispersed (left) and intact (right) material Y, cuttings recovery (%). White, H_2O Horizontal line, H_2O/KCl vertical line, PEG400 Black, PEG400/KCl.
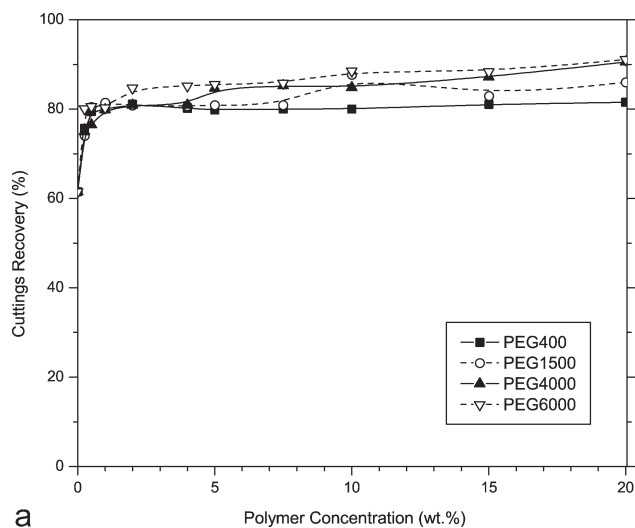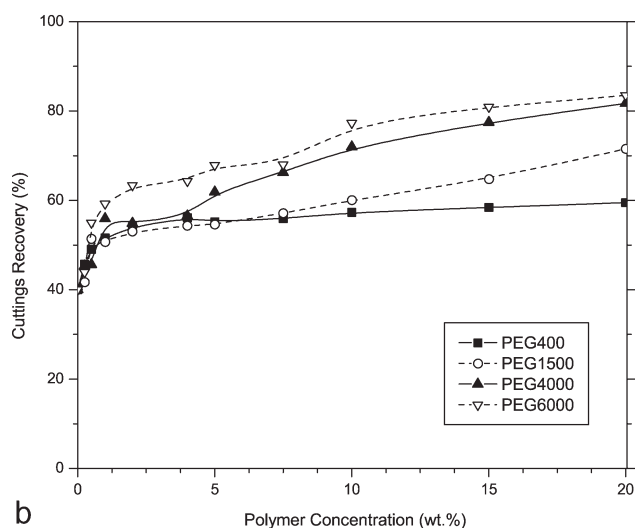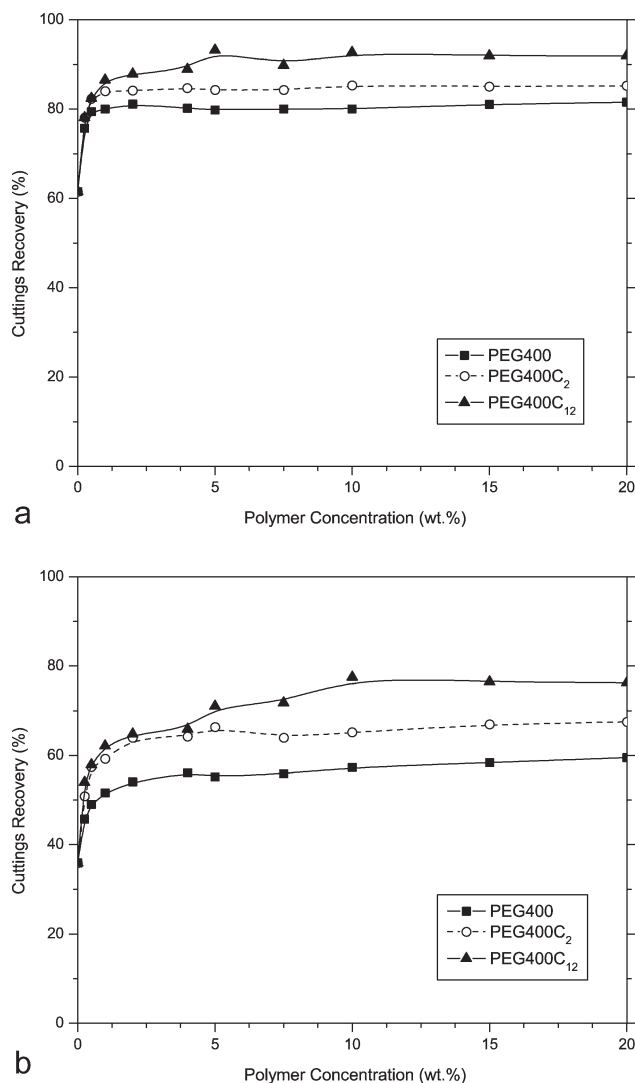
Figure 6 Cuttings recovery results obtained with PEGs in 3 wt % KCl solutions: (a) Dispersed Material X, polymer concentration (wt %) Y, cuttings recovery (%). Full symbol, straight line; empty symbol, dash line. (B) Cuttings recovery results obtained with PEGs in 3 wt % KCl solutions: (b) Intact Material X, polymer concentration (wt %) Y, cuttings recovery (%). Full symbol, straight line; empty symbol, dash line.

Dispersed and intact cuttings recovery results of clay treated with the PEGs, in the polymer concentration range of 0–20 wt %, are shown in Figure 6. All the unmodified polymers were able to enhance the dispersed cuttings recovery for at least 20% compared with the pure saline solution (control test) independently of the polymer concentration employed [Fig. 6(a)]. It is noted, however, that the intact cuttings recovery depends both on molar mass and on polymer concentration [Fig. 6(b)]. It is interesting to observe that a drawback of the unmodified polymers is the considerable amount of polymer needed to achieve high levels of intact cuttings recovery.

For unmodified polymers, which show no cloud point effect, increasing recovery is often attributed to the viscosity enhancement of polymer solutions,[12,13] however it cannot explain the fact that PEG400 can enhance the dispersed cuttings recovery. The cuttings rolling tests is a measure of the relative erosion of clay cuttings after contact with the fluid, it is clear that increasing the polymer concentration or the polymer chain length, thus increases the solution viscosity and the intact cuttings recovery. Moreover, the inhibition property may be also provided by the adsorption of polymer on clay particles. As shown by the adsorption experiments results, even low molecular weight PEG400 can be adsorbed on clay surface, competing with the water molecules for the active sites of the clay and hence stabilizing the cuttings. For the other PEGs, the adsorption becomes equally important and, as shown by the TGA results, these adsorbed polymers can displace water as efficiently as the PEG6000. The hydrophobically modified PEGs have lower phase separation temperature (cloud point) than the unmodified polymers, as previously reported,[38,39] and therefore they have lower solubility, which may increase the adsorption process, improving the inhibition property.

The cuttings recovery of hydrophobically modified PEGs is shown in Figure 7. The results show that inhibition properties of PEG are improved by hydrophobic modification. This hypothesis is supported by Reid et al. who have shown that terminal hydroxyl groups of the PEG's have no influence on the inhibition mechanism.[12] The dispersed cuttings recovery obtained with PEG400 dilaurate is similar to those obtained with an oil based fluid, i.e., up to 90% of recovery. In addition, the intact cuttings recovery results obtained with this diester was greater than those observed for unmodified polymers. This result is consistent with the usual effect of hydrophobic group substitution on the cloud point.[38,39] These hydrophobic groups act decreasing the polymer solubility and thus increasing the polymer adsorption.

The results for the cuttings rolling tests followed the same trend of the adsorption experiments with modified PEGs, suggesting that the clay/polymer interactions play an important role in the inhibition mechanism, despite the viscosifying effect cited before. Therefore, we consider that the most important contribution to clay inhibition comes from the adsorption properties of the modified PEGs, which is quite different from the ones obtained with unmodified polymers. The introduction of alkyl segments (laureate groups) in the polymer chain of the PEG enhances its affinity for the clay surface, as shown by the adsorption isotherms, as well as its ability to prevent water uptake, as shown by the TGA results. The interactions between these hydro-

Figure 7 Cuttings Recovery of Hydrophobically Modified PEGs in 3 wt % KCl solutions: (a) Dispersed Material X, polymer concentration (wt %) Y, cuttings recovery (%). Full symbol, straight line; empty symbol, dash line. (B) Cuttings Recovery of Hydrophobically Modified PEGs in 3 wt % KCl solutions: (b) Intact Material X, Polymer Concentration (wt %) Y, Cuttings Recovery (%). Full symbol, straight line; empty symbol, dash line.

phobic chains may lead to the formation of multiple layers of adsorbed polymer, which may be responsible for the preservation of the clay cuttings integrity. The formation of multiple layers of adsorbed polymer on the clay surface may physically block the pores and interlayers spaces, hindering the water entrance and thus minimizing the erosion of the clay particle during the contact test.

CONCLUSIONS

All the PEG polymers studied exhibit a low affinity adsorption isotherm type and the amount of

polymer adsorbed increased continuously with concentration. These polymers are able to penetrate into the interlamellar spaces of the clay. However, in the presence of potassium ions the entrance was limited to only one layer of polymer. The longer the unmodified polymer chain length, the greater the water amount displaced in the adsorption process.

The hydrophobic modification of PEG400 with long alkyl chain (lauric acid) significantly changed the adsorption behavior of the polymer, enhancing its affinity for the clay surface. The PEG400 dilaurate was able to intercalate in the basal spacing of the clay, keeping the alkyl chains outside the interlayers of the clay, blocking and preventing the water uptake by the clay. Therefore, it was able to inhibit the clay dispersion and disintegration, leading to more intact clay cuttings.

All PEGs studied are able to inhibit, in conjunction with KCl, the dispersion and disintegration of clay cuttings. The results clearly showed a qualitative correlation between the shale inhibition test results and the characteristics of the clay/polymer complexes obtained adsorption experiments. Optimum inhibition was reached when sufficient polymer has been adsorbed on clay to produce an ordered complex with 14 Å basal spacing, which minimized water uptake by the clay.

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