

Inhibitive Properties of Cationic Polymers in a Borehole Environment

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Received 27 June 2005; accepted 2 December 2005

DOI 10.1002/app.24168

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The adsorption behavior of poly(diallyldimethylammonium chloride) (PDADMAC) and of a copolymer with acrylamide on a native clay was studied as a function of the molecular weight of homopolymers, the ionic strength of the medium, and the ionic nature of the constituent blocks of the polymers. The clay was used without further purification or treatment in order to simulate a borehole environment. The properties of the clay–polymer systems studied were evaluated through total organic carbon analysis, thermogravimetric analysis (TGA), and X-ray diffraction analysis. The adsorption isotherms showed that all cationic polymers had high affinity for the clay, even in a highly saline medium and that the amount of polymer adsorbed strictly depended on the length of the macromo-

lecular chain. The TGA results showed that polymer adsorption was able to reduce the water content of the clay surfaces, independently of the molecular weight of the homopolymer. The inhibitive properties of the polycations were measured by conventional oilfield cuttings rolling tests, which showed that these polymers were able to reduce the dispersion and disintegration of the clay cuttings. The results also showed that inhibition was directly related to the clay–polymer interactions and, therefore, to the polymer structure. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2158–2163, 2006

Key words: adsorption; thermogravimetric analysis (TGA); polyelectrolytes; clay

INTRODUCTION

With the increasing environmental restrictions on the use of oil-based drilling fluids and their cuttings discharge, the demand for ecologically friendly water-based drilling fluids has increased in the last decade. Today, most of the world's petroleum drilling operations use water-based drilling fluids (WBFs).^{1,2} A major problem associated with the use of these fluids during perforation is the presence of shales containing smectite-rich clay minerals, which may swell and disintegrate in contact with water, leading to wellbore instability and drastic changes in the rheological properties of the mud. These shales are often encountered while drilling for oil and gas and cause more than 90% of wellbore instability problems.^{3–5}

To prevent degradation of the borehole and also the disintegration and dispersion of the drilled cuttings, different polymeric additives are used in WBFs, such as cationic polymers,^{6–8} hydrolyzed polyacrylamide,^{9,10} polyglycols,^{11,12} poly(amino acid)s,¹³ and polysaccharides.¹⁴ The inhibition capability of the drilling mud depends mainly on the water-soluble polymer used,

and the inhibition mechanism of any type of polymer is based on the type of clay–polymer interaction occurring. There are several possible mechanisms for this, depending on the nature of the polymer, and these mechanisms are not well understood yet.¹⁵ The adsorption of neutral polymers, for example, nonhydrolyzed polyacrylamide, on the clay's surface has been attributed to an entropic contribution that would arise from the displacement of water molecules by a single polymer chain or to an ion–dipole interaction like van der Waals forces, or even to segment–surface interactions, such as hydrogen bonding. In addition to that, the adsorption process may take place on the external and internal surfaces of the clay particles.^{16,17} The adsorption of anionic polymers [e.g., poly(acrylic acid)] on clays is limited by the electrostatic repulsion between the negative charges of ionized functional groups of the polymer and the negatively charged clay surfaces. In neutral solutions, the polyanions adopt an extended conformation because of the repulsion between the negative charges of the polymer. Thus, after the adsorption process, the polymer conformation is characterized by the presence of long tails, which favor interparticle bridging. The anionic polymers do not penetrate the interlayer space of the smectite clay, so adsorption is restricted to the external surface of the clay.^{16,18} The adsorption of cationic polymers, for example,

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poly(diallyldimethylammonium chloride) (PDADMAC), is a result of coulombic interactions between quaternary ammonium ions in the polymer and the negatively charged clay surface, neutralizing the anionic sites on the clay and leading to a reversal of the surface charge. Both the molecular weight and the charge of the polymers, as well as the ionic strength of the medium, influence the amount of polymer adsorbed, inasmuch as these factors influence the polymeric conformation in solution and also the interactions between clay particles, as previously reported.^{18,23} Cationic polyelectrolytes are widely used in the oil industry for many purposes, such as inhibiting corrosion and enhancing oil recovery and especially as additives for reactive shale inhibition in WBFs.²⁴ To evaluate the inhibitive properties of the mud, the oil industry often uses the cuttings rolling test, which evaluates the effect of the nature of the drilling fluid on the size of the shale cuttings after a period of contact. This test provides a quantitative estimation of the extent of intergranular cohesion and of the resistance to hydration forces and mechanical dispersion of shale cuttings after contact with the drilling fluid.^{25,27}

The present work studied the interactions of water-soluble polymers with smectite clay over a range of polymer concentrations. The purpose was to correlate the characteristics of the clay-polymer systems obtained such as adsorption isotherms and clay-water content with the inhibitive properties of the polymers. Therefore, the aim of this work was to study a series of PDADMAC homopolymers of different molecular weights and a copolymer with acrylamide (PDADMAC-co-AM) in order to evaluate how polymer structure and molecular weight influence the shale inhibition characteristics of cationic systems. For this purpose, clay was used without any further treatment or purification in order to simulate the conditions of a borehole. The same type of clay was used for the adsorption experiments and for the shale rolling tests.

EXPERIMENTAL

Materials

The cationic polyelectrolytes studied were poly(diallyldimethylammonium chloride)s (PDADMACs) of high (HMW), medium (MMW), and low (LMW) molecular weights, varying in the range from 100,000 to 500,000 Da, and a copolymer of PDADMAC with acrylamide (PDADMAC-co-AM). All polymers were characterized by ¹³C{¹H}-NMR, and all spectra were obtained on a Bruker Avance DPX-200 spectrometer at 75.5 MHz. All the polymer solutions were prepared in D₂O, the chemical shifts were reported relative to tetramethylsilane (the primary reference), and 1,4-dioxane was used as a secondary reference at

67.40 ppm. The polymers were all supplied by Sigma-Aldrich Company and were used without further purification.

The clay used in the adsorption experiments was a bentonite supplied by the Bentonorte Company (PB, Brazil); it was characterized by XDR, which showed that it was 45% smectite, 22% kaolinite, and 4% illite, as well as impurities, mainly quartz (20%) and calcite (5%). The clay was sieved to yield granules 23.6–4.76 mm in size, as recommended for the cuttings rolling test. An aliquot of less than 4.76 mm was ground in a ball mill for 10 h and then characterized and used in the adsorption experiments. The surface area of the solids, as determined by Brunauer-Emmet-Teller (BET) nitrogen adsorption, was 32.76 m²/g. Particle size, $x_{50} = 2.09 \mu\text{m}$, was measured with a Quantachrome Microscan II analyzer.

Methods

Adsorption experiments were run, adding 14 g of clay to a polymer solution of a known concentration. The solutions were shaken in a water bath at 32°C for 16 h, followed by centrifugation to settle the solids. Then the samples were dried at 100°C, ground, and stored in sealed flasks. The amount of polymer adsorbed on the clay was determined by total organic carbon analysis using a Leco CS-444 apparatus. The water content of the clay-polymer systems was determined by thermogravimetric analysis using a Shimadzu TGA-51 apparatus, with a heating rate of 10°C/min under an N₂ atmosphere. The samples for X-ray diffraction (XRD) studies were ground to less than 50 μm and deposited as slurries on glass slides and then air-dried. The XRD data were obtained on a Siemens/Brucker AXS-D5005 X-ray Diffractometer using Cu K α radiation and collected stepwise at 0.01° (2 θ) from 2° to 10° (2 θ) with a time of 2 s per step. For the cuttings rolling tests the procedure of Beihoffer²⁷ slightly modified was followed. Fifty grams of the sized clay was 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 collected on a 0.12-mm sieve, called dispersed material, was washed with distilled water. The clay was then collected on a 4.76-mm sieve in order to evaluate the percentage of material that maintained its original size, referred to as intact material. The cuttings were then dried to a constant weight in an oven at 100°C. The percent recovery of clay, after correcting the original mass for the water content of the clay (9.8%), was calculated on a dry mass basis as follows:

$$\%R = W/W_0 \times 100$$

where W and W_0 are the weight after and before rolling, respectively.

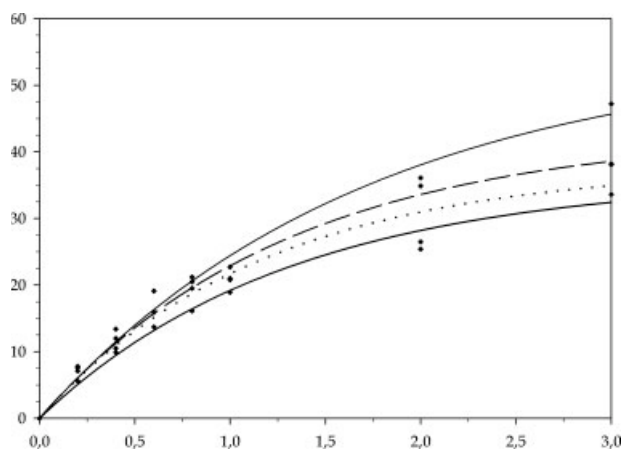


Figure 1 Adsorption isotherms of PDADMAC polymers on clay { X = initial polymer concentration [% (p/v)], Y = adsorbed mass (mg polymer/g clay); — PDADMAC-HMW, PDADMAC-MMW, --- PDADMAC-LMW, - · - · - PDADMAC-co-AM}.

RESULTS AND DISCUSSION

Adsorption

All clay-polymer systems studied presented adsorption isotherms of the H type (Fig. 1), indicating a strong affinity between the polymer and the clay, as expected for polymer adsorption on oppositely charged particles.²⁰ All adsorption data were analyzed according to the linearized Langmuir equation.²⁸ The mass of adsorbate per gram needed to form a monolayer (N_m) was obtained plotting the equilibrium concentration (C_e) versus C_e/N , where N is the mass of adsorbate per gram of clay at some equilibrium concentration (C_e), yielding a straight line with a slope of $1/N_m$. Table I lists the results of the adsorption experiments and gives the values of N_m for all polymers in nonsaline and saline media and their respective correlation coefficient.

Table I shows that the adsorption process was dependent on the molecular weight of the cationic polymers. The PDADMAC-HMW system showed the lowest adsorption because the intercrystalline (pores) and intracrystalline (interlayer) spaces of the clay system may be physically inaccessible to macromolecules above a certain size. The similarity of the adsorption isotherms suggests a single adsorption mechanism for these polymers based on electrostatic interactions between the quaternary ammonium ions in the polymers and the negatively charged surface of the clay, as reported previously.¹⁶ The copolymer with acrylamide showed an adsorption isotherm similar to that of other cationic polyelectrolytes, suggesting the adsorption process was governed by the cationic fraction of the macromolecule.

The adsorption process was dependent on, among other factors, the ionic strength of the medium and

the clay concentration.²⁰ The presence of electrolytes reduced the intramolecular charge repulsion between the functional groups of the polymer, leading it to having a random coil conformation. On the other hand, an increase in the ionic strength of the medium suggested there was a decrease in the electrostatic repulsions between clay platelets because of the screening of negative surface charges, favoring the face-to-face association of particles and, thus, aggregation phenomena. As shown on Table I, increasing the ionic strength led to a small decrease in the polymer adsorption, suggesting that with a high concentration of clay, the adsorption process was strongly influenced by the interactions between the clay particles.

TGA

Thermogravimetric analysis (TGA) of all the clay-polymer systems showed they all had the same characteristic profile of a thermogram for a clay mineral of the smectite group, with two losses of mass: the first associated with the water adsorbed on the interlamellar and external surfaces, at 20°C–300°C (dehydration), and the second associated with the structural hydroxyl groups from the octahedral layer, at 450°C–700°C (dehydroxylation).²⁹ The present study focused on the mass loss in the range of 20°C–300°C because it is well known that water content plays an important role in clay reactivity. As shown in Figure 2, all cationic polymers were able to reduce the water content of the surface of the clay, an effect that became larger as polymer concentration increased. This finding agreed with the carbon analysis results, which showed that polymer adsorption increased with polymer concentration (Fig. 1), leading to a decrease in the hydrophilicity of the mineral surface and, consequently, reducing its water content. Nevertheless, the thermogravimetric analysis was not able to distinguish the cationic homopolymers by molecular weight. The copolymer containing acrylamide showed a greater capacity to reduce water content than the homopolymers, which could be attributed to adsorption of both the cationic and the nonionic blocks of the macromolecules. As suggested by the adsorption isotherms (Fig. 1), adsorption by the copolymer could be governed mainly by the cationic fraction of the molecule, which

TABLE I
Maximum Amount of Polymer Adsorbed (N_m)

Polymer	N_m (mg/g)			
	Nonsaline	R (95%)	Saline	R (95%)
PDADMAC-HMW	42	0.9813	38	0.9557
PDADMAC-MMW	49	0.9842	37	0.9681
PDADMAC-LMW	60	0.9577	43	0.9703
PDADMAC-co-AM	46	0.9560	35	0.9511

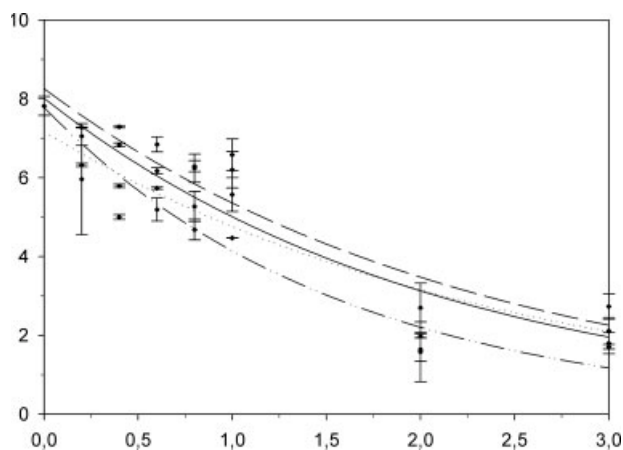


Figure 2 Mass loss in the 20°C–300°C range for adsorption in a nonsaline medium {X = polymer concentration [% (p/v)], Y = mass loss at 30°C–200°C (%); — PDADMAC-HMW, PDADMAC-MMW, — — — PDADMAC-LMW, — · — · — PDADMAC-co-AM}.

would be neutralizing the negative sites on the clay surface, whereas the coiled polyacrylamide portion could be partially adsorbed on the edges of the clay, hindering entry of water molecules into the porous and interlayer domains.

The behavior of and interactions between individual clay particles in an aqueous suspension depend on clay concentration, particle size, type of exchangeable cation, and ionic strength of the medium.^{16,30} The inclusion of potassium chloride in the adsorption experiments led to clay–polymer systems with a reduced water content, as shown in Figure 3, even with low polymer concentrations. As already mentioned, an increase in salinity can reduce polymer adsorption because the internal surfaces of a clay sheet may become inaccessible to macromolecules.

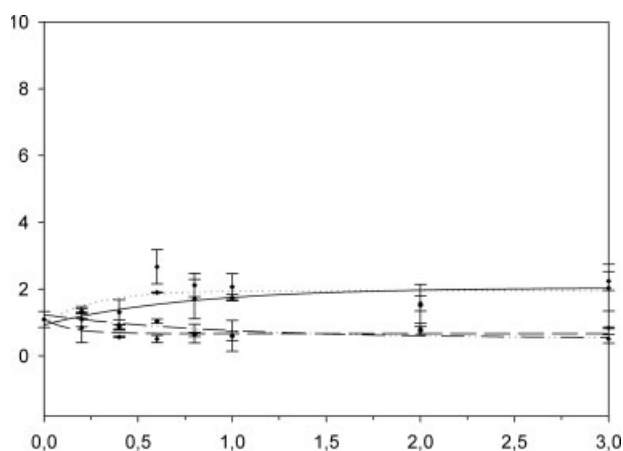


Figure 3 Mass loss in the 20°C–300°C range for adsorptions in a saline medium {X = polymer concentration [% (p/v)], Y = mass loss at 30°C–200°C (%); — PDADMAC-HMW, PDADMAC-MMW, — — — PDADMAC-LMW, — · — · — PDADMAC-co-AM}.

DRX

Numerous factors affected the basal spacing of the smectite, including type of cation in the interlayer region and relative humidity.³¹ Table II lists the results from the adsorption experiments for basal spacing (001) of the clay–polymer systems in conditions of a nonsaline solution and of a potassium chloride solution.

The clay (blank) in the neutral solution showed a d_{001} spacing of a montmorillonite, with an uptake of two water molecules in the interlamellar region, suggesting this sample was not correctly protected from the external humidity. Nevertheless, the basal spacing observed for the PDADMAC/clay systems (15.5 Å) was characteristic of the presence of one layer of polymer in the interlamellar spaces of the clay’s sheets.³² This behavior was in agreement with the results of the adsorption and thermogravimetric analyses, as the polymer molecules adsorbed could have been hindering the water molecules from entering the interlayer regions, reducing the water content of the systems.

At high clay concentrations the particles preferentially consisted of face-to-face associations of platelets, and with the addition of salt, that is, in high ionic strength, the number and the size of these aggregates were enhanced.^{20,30} Despite the drastic modification of the mean distance between particles, it was possible to accept that, to some extent, polymer adsorption in the interlayer domain was occurring because the basal spacing reflection of these clay–polymer systems was larger than that of the respective control. However, for PDADMAC-HMW two distinct basal spacing reflections were observed, which may be attributed to the longer polymer chain that would have been forming a film on the external surfaces of the clay aggregates. Thus, basal spacing reflections not only for the polymer adsorbed on the external surface but also for the clay that was inaccessible to the polymer (internal domain) would be observed.

Cuttings rolling tests

All polycations were tested at a concentration in the range of 0.1%–1.0% (p/v) in distilled water. The polymers were also tested at a concentration of 1.0% (p/v)

TABLE II
Basal Spacings (001) for Clay–Polymer Systems

Polymer	d_{001} (Å)	
	Nonsaline medium	Saline medium
Blank	15.6	12.5
PDADMAC-HMW	15.5	13.5 and 16.0
PDADMAC-MMW	15.5	14.4
PDADMAC-LMW	15.3	14.6
PDADMAC-co-AM	14.6	14.3

in a 10% (p/v) solution of KCl. These results were compared to those obtained with the controls with distilled water and a potassium chloride solution.

All cationic polymers were able to inhibit dispersion and disintegration of the clay granules, as shown in Figures 4 and 5. Clay recovery increased exponentially, tending toward a plateau region (Fig. 4), for polymeric concentrations greater than 0.5% (p/v). This seems to agree with the adsorption results, as the amount of polymer adsorbed on the clay tends to have a defined value, N_m , which corresponds to monolayer formation. Because in salt-free solutions the polymers behaved as strongly charged rodlike polycations in, it was expected that the adsorbed polymers would adopt a flat configuration. However, if the clay surface was near saturation, polymer adsorption would become hindered, forming long tails that would bridge individual clay particles, bringing more cohesion to the clay. The test results did not differentiate the individual homopolymers by molecular weight, so either the clay was not reactive enough to distinguish among them or the test itself was not adequate for this purpose.

In contrast, the recovery curves of the intact material (> 4.76 mm) showed that the cationic copolymer with acrylamide was the best inhibitor of clay (Fig. 5). These results provided support for the hypothesis that there were two distinct adsorption mechanisms acting simultaneously, one associated with the cationic block and the other with the acrylamide block. The copolymer was strongly adsorbed because of the cationic block, which neutralized the anionic sites on the clay surface, whereas the nonionic block adsorbed on the external surface (edges) because of less selective interactions like van der Waals forces and hydrogen bond-

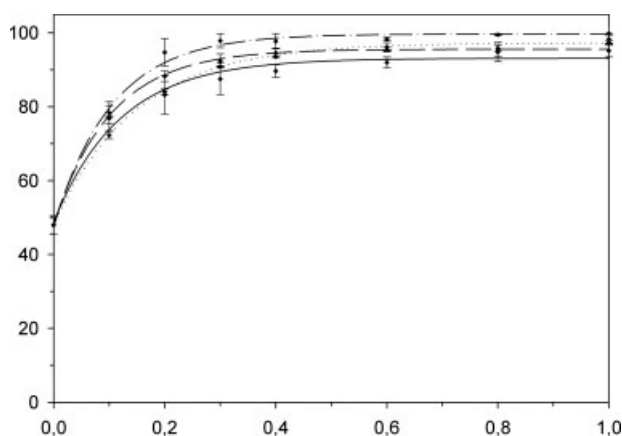


Figure 4 Recovery of cuttings greater than 0.12 mm (U.S. mesh 30) as a function of polycation concentration in a nonsaline medium [X = polymer concentration [% (p/v)], Y = cuttings recovery (dispersed material) (%); — PDADMAC-HMW, PDADMAC-MMW, --- PDADMAC-LMW, - · - · - PDADMAC-co-AM].

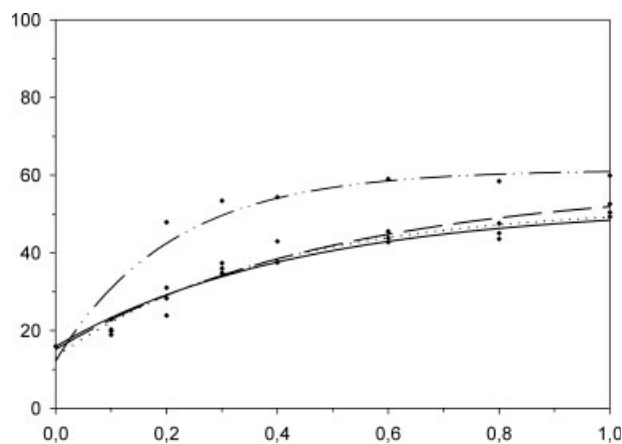


Figure 5 Recovery of cuttings greater than 4.76 mm as a function of polycation concentration in a nonsaline medium [X = polymer concentration [% (p/v)], Y = recovery of cuttings, that is, intact material (%); — PDADMAC-HMW, PDADMAC-MMW, --- PDADMAC-LMW, - · - · - PDADMAC-co-AM].

ing. On a clay surface polycations can form a film, with coiled nonionic blocks projecting outside the surface. In this situation, the polymer adsorbed might lubricate particle contacts, contributing to decreased erosion of the granules.

CONCLUSIONS

The results of the adsorption experiments suggest that different cationic polymers were adsorbed via the same adsorption mechanism, even in a highly saline medium. The adsorption isotherms clearly showed that even for the native clay used the length of the macromolecular chain depended on the adsorption in porous adsorbents. All the polymers studied were able to greatly modify the clay surface, reducing the hydrophilicity and, thus, reducing the amount of water adsorbed on the clay surface. However, in potassium chloride solutions, the water content of the samples was independent of polymer concentration and was lower than that observed in the nonionic solutions. The DRX results showed that in a highly ionic medium, basal spacing was reduced because potassium ions were easily accommodated in the hexagonal network of oxygen atoms on the clay sheets, bringing them close together.

The adsorption behavior of the PDADMAC polymers seems to have had a direct relation to their inhibitive effect on native clay granules. Even with a low polymer concentration, adsorption was high enough to prevent the disintegration and dispersion of the clay cuttings. However, the copolymer containing acrylamide showed by far the best results for intact material recovery. The cationic copolymer would be adsorbed on the clay, encapsulating the pellets and sealing the porous and interlamellar domains; this

would minimize clay–water interactions and therefore reduce clay swelling.

The authors are grateful to Edimir Brandão and Sebastião Oliveira, CENPES/PETROBRAS, for useful comments on the inhibition tests.

References

1. Bland, R. G.; Clapper, D. K.; Fleming, N. M.; Hood, C. A. Presented at the IADC/SPE Drilling Conference, Amsterdam, 1993; SPE paper 25754.
2. Caenn, R.; Chillingar, G. V. *J Pet Sci Eng* 1996, 14, 221.
3. Mody, F. K.; Hale, A. H. *J Pet Technol* 1993, 45, 1093.
4. Durand, C.; Forsans, T.; Ruffet, C.; Audibert, A. *Rev Instit Français Pétrole* 1995, 50, 187.
5. Bloys, B. *Oilfield Rev* 1994, April, 33.
6. Strickland, S. D. *J Petrol Technol* 1994, August, 691.
7. Stamatakis, E.; Thaemlitz, C. J.; Coffin, G.; Reid, W. Presented at the IADC/SPE Drilling Conference, Amsterdam, 1995; SPE paper 29406.
8. Schmidt, D. D.; Beihoffer, T. W.; Dorrough, D. S.; Deem, C. K. *Oil Gas J* 1992, March, 47.
9. Kadaster, A. G.; Guild, G. J. Presented at the SPE/Annual Technical Conference and Exhibition, San Antonio, TX, 1989; SPE paper 19531.
10. Bol, G. M. Presented at the IADC/SPE Drilling Conference, Dallas, TX, 1986; SPE paper 14802.
11. Mpofu, P.; Mensah, J.; Ralston, J. *Miner Eng* 2004, 17, 411.
12. Aston, M. S.; Elliott, G. P. Presented at the SPE/European Petroleum Conference, London, 1994; SPE paper 28818.
13. Bruton, J. R. Presented at the SPE Annual Technical Conference and Exhibition, Houston, TX, 1993; SPE paper 26237.
14. Zhang, L. M.; Tan, Y. B.; Li, Z. M. *Colloid Polym Sci* 1999, 277, 1001.
15. Theng, B. K. *Clays Clay Miner* 1982, 30, 4.
16. Theng, B. K. *Formation and Properties of Clay–Polymer Complexes*; Elsevier Publishing: New York, 1979; Chapter 1.
17. Bailey, L.; Keall, M. *Langmuir* 1994, 10, 1544.
18. Breen, C.; Rawson, J. O.; Mann, B. E. *J Mater Chem* 1996, 6, 253.
19. Billingham, J.; Breen, C.; Rawson, J. O.; Yarwood, J.; Mann, B. E. *J Colloid Interf Sci* 1997, 193, 183.
20. Petzold, G.; Buchhammer, H. M. *J Appl Polym Sci* 2000, 75, 16.
21. Ueda, T.; Harada, S. *J Appl Polym Sci* 1968, 12, 2395.
22. Kokufuta, E.; Takahashi, K. *Macromolecules* 1986, 19, 351.
23. Kriz, J.; Dybal, J.; Kurkova, D. *J Phys Chem* 2002, 106, 7971.
24. Hemphill, T.; Valenziano, R.; Bale, P.; Sketchler, B. *Oil Gas J* 1992, June, 60.
25. Chenevert, M. E.; Osisanya, S. O. *SPE Drill Completion* 1989, September, 261.
26. Osisanya, S. O.; Chenevert, M. E. Presented at the SPE/IADC Drilling Conference, New Orleans, LA, 1987; SPE paper 16054.
27. Beihoffer, T. W.; Dorrough, D. S.; Schmidt, D. D. Presented at the IADC/SPE Drilling Conference, Texas, 1990; SPE paper 19953.
28. Giles, C. H.; Smith, D.; Huitson, A. *J Colloid Interf Sci* 1974, 47, 755.
29. Fajnor, V. S.; Jesenak, K. *J Therm Anal* 1996, 46, 489.
30. Luckham, P. F.; Rossi, S. *Adv Colloid Interfac Sci* 1999, 82, 43.
31. Grim, R. E. *Clay Mineralogy*; McGraw-Hill: New York, 1968; Chapter 6.
32. Billingham, J.; Breen, C.; Yarwood, J. *Vib Spectrosc* 1997, 14, 19.