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ANIONIC POLYACRYLAMIDE POLYMER ADSORPTION BY PYROPHYLLITE AND MONTMORILLONITE

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Abstract—The mechanism by which the anionic polymers interact with platelets of 2:1 clay minerals is not fully understood. The objective of the present study was to evaluate the effect of the electric field associated with the basal and edge surfaces of the clay minerals on the adsorption of anionic polymers. Two negatively charged polymers, PAM90 and ACC86, of the same molecular weight (2×10^5 g mol^{-1}) but with different degrees of hydrolysis (90 and 20%, respectively), were used. The effect of pH (6, 10), NaCl concentration (0, 10 $mmol_C$ L^{-1}) and clay particle size on PAM90 adsorption by pyrophyllite and the effect of NaCl concentration on the adsorption of these polymers by Na-montmorillonite in aqueous suspensions were studied. Adsorption of PAM90 on pyrophyllite was greater at pH 6 than at pH 10 and greater in 10 mmol L^{-1} NaCl than in distilled water. Adsorption of PAM90 on pyrophyllite increased with decreasing particle size. On pyrophyllite the high-charge-density PAM90 was adsorbed to a greater extent than the low-charge-density ACC86; by contrast, ACC86 adsorption was greater than that of PAM90 on Na-montmorillonite. These results were attributed to the repulsive forces which develop between the negatively charged extended-chain polymer and the extended negative electric field associated with the basal surfaces, around the Na-montmorillonite platelets. The results may suggest that the edge surfaces play a major role in PAM adsorption.

Key Words—Montmorillonite, Polyacrylamide-Clay Interaction, Pyrophyllite.

INTRODUCTION

Since Ruehrwein and Ward (1952) suggested that anionic polymers can flocculate clay suspensions by forming interparticle bonds, extensive work has been carried out on polymers-clay particle interactions, as related to flocculation and adsorption (van Olphen, 1977; Theng, 1979). The promotion of flocculation of soil clay, kaolinite, illite and montmorillonite by a high-molecular-weight anionic polymer such as polyacrylamide (PAM) was observed by Black *et al.* (1965); Aly and Letey (1988) and Laird (1997). This phenomenon depends on the polymer properties such as molecular weight (MW) and the degree of hydrolysis (DH). The higher the MW and the DH, the greater the interparticle bond formation and, therefore, the greater the ability to promote clay particle flocculation (Greenland, 1972; Theng, 1979). Anionic PAM (with a low DH of 18%) was more effective at flocculating Na-kaolinite than Na-illite (Laird, 1977).

Recently, Heller and Keren (2002) observed that the presence of an anionic PAM modified the flow behavior of Na-montmorillonite suspensions, and that the viscosity was affected by the MW, DH and electrolyte concentration. In the absence of an electrolyte, only the largest polymer could form a three-dimensional network, whereas the smallest polymer prevented particle-particle association. The greatest influence of the polymers on the flow behavior of clay suspensions was obtained when the electrolyte (NaCl) concentration was 10 $mmol_c$ L^{-1}, at which the attractive forces between montmorillonite platelets were very weak (Heller and Keren, 2001). The effect of the polymers increased with increasing MW and DH. Thus, as was previously indicated, polyanions can act as effective flocculating agents of clay in suspensions, despite the fact that both the polymer and the suspended particles carry a net negative electrostatic charge.

The adsorption capacity of clay minerals for anionic PAM depends on the clay type (*e.g.* the adsorption capacity of illite is greater than that of montmorillonite (Ben-Hur *et al.,* 1992)) as well as on the characteristics of the polymer and of the ambient solution. The adsorption of PAM by kaolinite increased with salinity (NaCl) and decreased as pH increased from 4 to 6 (Lee *et al.*, 1991) but no effect was observed in the pH range 6 to 10. At pH >10, adsorption decreased markedly, to negligible values. It was concluded that the effect of solution electrolyte concentration and pH on the adsorption of anionic PAMs on kaolinite and Na-montmorillonite is due to the decrease in the electrostatic repulsion forces between the polymer molecules and the mineral surfaces (Lee *et al.*, 1991; Aly and Letey, 1988). It was also suggested that cation bridging (PAM-Ca-clay) is a possible bonding mechanism between anionic PAMs and clay mineral surfaces (Stutzmann and Siffert, 1977).

Conflicting results from PAM adsorption by Na-montmorillonite have been published. An increase in the

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polymer DH (in the range 15–25%) resulted in a significant increase in adsorption by Na-montmorillonite (Stutzmann and Siffert, 1977; Espinasse and Siffert, 1979) whereas Aly and Letey (1988) observed that anionic PAM adsorption by Na-montmorillonite decreased as the charge density of the polymer increased. The retention of the polymer on montmorillonite in an irreversible adsorption process was low (3 mg g^{-1}), but increased with the cation exchange capacity (CEC) of the clay mineral (Stutzmann and Siffert, 1977).

Although anionic PAM was effective at promoting clay flocculation and at modifying the flow behavior of Na-montmorillonite suspensions, the mechanism by which the anionic polymers interact with clay platelets is not fully understood. Based on the results obtained so far, five possible mechanisms for the fixation of polyelectrolytes on kaolinite and montmorillonite surfaces have been proposed (Michaels and Morelos, 1955; Stutzmann and Siffert, 1977; Laird, 1997): (1) ligand exchange between the surface hydroxyls of the mineral and the carboxylic anions of the polymer; (2) the formation of hydrogen bonds between the surface hydroxyls and the polymer C=O groups; (3) divalent cations forming bridges between negative charge sites on the clay surfaces and carboxylate groups on the anionic PAM; (4) generation of protons on the edge surface of the clay crystallites by the polarization of the water molecules in contact with the exchangeable cations of the clay, followed by transfer of hydrogen to the amide groups, and adsorption of the polymer on the resulting protonated sites; and (5) hydrophobic bonding between the carbon chain of the anionic PAM and the uncharged basal surfaces of the clay.

The clay mineral pyrophyllite consists of essentially neutral tetrahedral-octahedral-tetrahedral sheets. Since the basal surfaces of pyrophyllite are uncharged and the edge surfaces have similar properties to those of the rest of the phyllosilicates, such as pH-dependent surface charge and electric potential, anionic PAM adsorption on this clay may provide additional information on the active sites of montmorillonite involved in adsorption. The objective of the present study, therefore, was to evaluate the effect of the electric field associated with the basal and the edge surfaces of the clay minerals on the adsorption of anionic PAMs.

MATERIALS AND METHODS

Clay preparation

The <2 μm fraction of montmorillonite from Osage, Wyoming was extracted by allowing larger particles in the clay suspension to settle in distilled water (as calculated by Stokes' law), and then decanting. The Na-clay was prepared by leaching the clay fraction three times with 1 mol_c L^{-1} NaCl solution, and then leaching the clay with distilled water and separating in a high-speed centrifuge until the solution was free of Cl^-. Chloride was considered to be absent when the supernatant liquid gave a negative test with $AgNO_3$. The salt-free clay was freeze dried and stored in a desiccator over P_2O_5.

Pyrophyllite (Robbins, NC, obtained from Ward's Natural Science Establishment, Inc.) was selected to simulate montmorillonite clay with very low electrostatic charge associated with this clay's basal surfaces (Bleam *et al.*, 1993; Okuda *et al.*, 1996). The mineral was ground in a porcelain ball mill (Coors, USA) containing zirconia balls (1.27 cm in diameter) for 30 h to increase the <2 μm clay fraction in the clay powder. The <2 μm clay fraction was obtained by allowing larger particles to settle in aqueous suspension and then decanting the suspension containing the <2 μm clay fraction. The clay was leached with 0.5 mol_C L^{-1} NaCl solution at pH 7 and then leached with distilled water, as above. The suspension was then freeze dried and kept in a desiccator over P_2O_5.

Part of the pyrophyllite suspension was treated with an ultrasonic vibrator (USV) (model Sonifier B-12A, Branson Sonic Power Co.) for 45 min at 50 W. A probe-type instrument in which the magnetostrictive oscillation is transmitted to the sample by means of a Ti probe was used. The temperature of the suspension was maintained at 23±1°C by a water jacket. The treated clay was centrifuged for 30 min at $2030 \times g$ (Beckman model J2-21M Induction Drive Centrifuge with JA17 rotor) to obtain suspensions with particles <0.02 μm. The settled clay particles were re-suspended and centrifuged for 30 min at $600 \times g$ to separate clay particles in the size range, 0.02–0.2 μm, which remained in the supernatant liquid, from particles in the 0.2–2.0 μm range, which settled. A clay suspension at a concentration of 0.2% w/w was prepared from each particle-size fraction. The light transmission of 0.05% clay suspensions (obtained by dilution of the 0.2% w/w clay suspensions with distilled water) for the various particle-size fractions was determined with a Varian Techtron UV-VIS Spectrophotometer, model 635 at a wavelength of 550 nm. The light transmittance of the particle-size fractions <0.02, 0.02–0.2 and 0.2–2.0 μm in suspension at pH 8.3±0.2 were 73.2, 71.9 and 8.2%, respectively.

Polymers

Two anionic polyacrylamides (co-polymers of polyacrylamide and polyacrylic acid) were used: (1) ACC86 (Cyanamid B.V., Rotterdam, The Netherlands); and (2) PAM90 (Aldrich Chemical Company, Inc. USA). The two polymers had the same MW of 2×10^5 g mol^{-1} but differed in their DH: 20% and 90%, respectively. The polymers were labeled with tritium by catalytic exchange with labeled water at high tritium concentration, for 120 h at room temperature (Rotem Industries Ltd., Israel). The labeled ACC86 and PAM90 polymers had specific activities of 2.78 and 1.0 mCi/mg (1.0 and

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1.9 mCi/mL), respectively, and were kept in aqueous solution at a temperature of 4ºC. Since the labeled polymers were kept in aqueous solutions, some activity loss was expected because of tritium exchange reactions between the polymer and water molecules. Activity losses of 8 and 14% were obtained for ACC86 and PAM90 polymers, respectively, during the equilibration time of 24 h at the same temperature at which PAM adsorption took place.

Adsorption procedure

The adsorption measurements were conducted by adding a polyacrylamide solution of a mixture of unlabeled and labeled polyacrylamides. 20 μL of labeled polymer were added to 250 mL of unlabeled polymer at a concentration of 800 mg L^{-1}. The amounts of the labeled polymers added were negligible in comparison to the unlabeled polymers in the 250 mL solutions (the concentration of the polymers was changed by <0.01%).

These solutions were diluted to obtain the final desired PAM concentrations in the clay suspension (the highest PAM concentration was 100 mg L^{-1}). The final clay suspension concentrations were 22.5, 10.0 or 1.0 g L^{-1}. The electrolyte NaCl, when present, was added to the clay suspension before the labeled polymer solution. The pH values of the clay suspension and of the polymer solutions were adjusted separately by adding dilute NaOH or HCl solutions.

The suspensions were shaken for 24 h at a temperature of 24.5±1.5ºC. After the equilibration interval, the suspensions were centrifuged and an 0.5 mL aliquot of supernatant liquid from each tube (in three replicates) was transferred to a 7 mL scintillation vial containing 4 mL of Ultima Gold LSC-cocktail (Packard, USA). The tritium activity was determined with a Packard Tri-Carb Beta counter (model BPL, Packard Instrument Company Inc., USA). The amount of adsorbed polymer was calculated as the difference between the amount added and that determined in the equilibrium solution. The loss of tritium activity from polymer to water was taken into account in the sorption calculations.

RESULTS AND DISCUSSION

The PAM90 adsorption isotherms on pyrophyllite at pH 6 and 10 and at solution NaCl concentrations of 0 and 10 $mmol_C$ L^{-1} are given in Figure 1. The linear shape indicates that the fraction of occupied adsorption sites is small, compared with the adsorption capacity of the clay. The PAM90 adsorption by pyrophyllite decreased as the pH increased and the NaCl concentration decreased.

The most pronounced pH effect was observed when no NaCl was added to the suspension (Figure 1a). The adsorbed polymer concentration at any equilibrium solution concentration decreased as the pH increased from 6 to 10, and the slope of the adsorption isotherms decreased from 0.12 to $4x10^{-3}$ L g^{-1} as the pH increased from 6 to 10.

The mechanism by which cations form bridges between negative charge sites on the clay surfaces and carboxylate groups on the anionic PAM is hardly possible for pyrophyllite because of the very low negative electrostatic charge associated with the basal surfaces (Bleam *et al.*, 1993; Okuda *et al.*, 1996). If adsorption occurs on the basal surfaces of pyrophyllite, then the hydrophobic bonding between the carbon chain of the anionic PAM and the uncharged basal surface sites could be the mechanism as suggested by Laird (1997). It is also possible, however, that hydrogen bonding involving the silanol groups may contribute substantially to the retention of PAM at pH 6 but is ineffective at pH10.

Another possibility is that the adsorption sites are also located on the edge of the clay surfaces as suggested by Theng (1982). Since the pH and the NaCl concentration have no effect on the properties of the pyrophyllite basal surfaces, the significant effect of pH and NaCl concentration on PAM90 adsorption by this clay may suggest that the edge surfaces play a major role in PAM adsorption.

This pH effect can be explained in terms of the electric properties of the pyrophyllite edge surfaces and the electrostatic charge and structural shape of the polymer. Anions adsorb to sites located on the phyllosilicate crystal edges of the clay, either through electrostatic interactions with positive charges on the

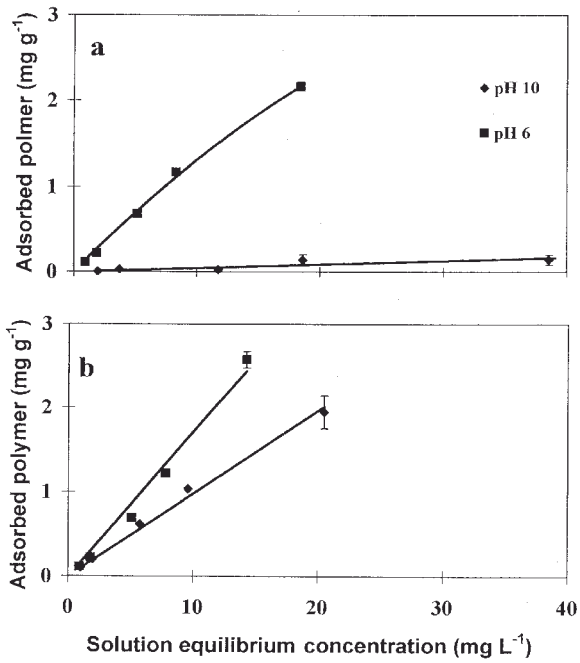


Figure 1. The effects of suspension pH and electrolyte concentration on PAM90 adsorption by pyrophyllite in clay suspension at a concentration of 10 g L^{-1}. (a) no added NaCl, and (b) 10 $mmol_C$ L^{-1} NaCl.

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edges or by a ligand-exchange mechanism with structural OH^- groups (Lagaly, 1987; Theng, 1979). The functional group on the edge surfaces is the hydroxyl exposed on the outer periphery of the clay mineral; it is associated with two types of sites that are available for adsorption, Al(III) and Si(IV), which are located at the octahedral and tetrahedral sheets, respectively. The OH group associated with these sites can form an inner-sphere surface complex with a proton or with a hydroxyl. Thus, the net electrostatic charge can be either negative or positive, depending on whether the suspension pH is above or below the point of zero salt effect (PZSE), respectively. The edge surfaces of pyrophyllite have similar properties to those of the rest of the phyllosilicates, such as pH-dependent surface charge and anion exchange capability. The PZSE of the edge surfaces of pyrophyllite is 4.2 (Keren and Sparks, 1995). At pH 6, the surface negative electric potential is relatively low (110 mV, Keren and Sparks, 1995), and it decreases with distance, perpendicular to the surface. The presence of a weak electric field around the edge surface makes the edges more accessible to an approaching negatively charged PAM.

The adsorbed polymer concentration on pyrophyllite decreased significantly as the pH increased from 6 to 10 (Figure 1a). The low adsorption level at the latter pH was probably due to competition with OH^- on the adsorption sites as well as the increase of the surface negative electric potential on the edges to 350 mV (Keren and Sparks, 1995). Under these conditions the repulsive forces acting between the negative charge of the polymer and that of the edge surface increased significantly, making the latter less accessible to approaching negatively charged PAM.

When the solution NaCl concentration increased to 10 $mmol_c\ L^{-1}$, the slope of the adsorption isotherms at pH 10 and 6 increased significantly (Figure 1b). At pH 10, the slope increased from $4x10^{-3}$ to $9x10^{-2}$ L g^{-1} as the solution electrolyte concentration increased to 10 $mmol_c\ L^{-1}$. These results suggest that a NaCl concentration of 10 $mmol_c\ L^{-1}$ was high enough to compress the diffuse double layer (which is associated with the edge surfaces). The calculated absolute value of the electric potential associated with the edge surface supported the experimental results. The electric potential value fell sharply at short distances from the edge surface, and the rate of decrease increased as the NaCl concentration was increased (Keren and Sparks, 1994). Thus, the adsorption capacity of the pyrophyllite for PAM90 under these conditions was greater than that observed for the suspension when no NaCl was added. Similarly, an increase in PAM90 adsorption was observed for pH 6 but to a lesser extent, since the negative electric field associated with the edge surface is weaker than that at pH 10.

The adsorption isotherms of PAM90 polymer on pyrophyllite, in three particle size ranges (0.2–2.0, 0.02–0.2 and <0.02 μm) are presented in Figure 2. In general, the polymer adsorption per unit weight of pyrophyllite increased as the particle size decreased. Based on the light transmittance measurements, the fraction of the edge surface area, in relation to the total surface area of the clay, increases as the clay-particle size decreases because of the reduction in particle size. The findings that the amount of adsorbed polymer increased as the clay-particle size decreased, and that the polymer adsorption by the larger clay particles (0.2–2.0 μm) approached the adsorption capacity, also supports the hypothesis that the negatively charged PAM polymers are adsorbed on the edge surfaces of the clay.

The adsorption isotherms of negatively charged PAMs of the same MW but having differing DH values (PAM90 – high DH; ACC86 – low DH), on pyrophyllite and Na-montmorillonite, in the absence of free electrolytes are presented in Figure 3. The lower amount of polymer adsorption by pyrophyllite than that observed for the same clay shown in Figures 1 and 2 is due to the difference in suspension clay concentration (Lee *et al.*, 1991). The differences between pyrophyllite and montmorillonite clays are in their specific surface area (44 and 800 $m^2\ g^{-1}$, respectively, Keren and Sparks, 1995), and electrostatic charge density (3×10^{-3}, Okuda *et al.*, 1996, and 0.117 C m^{-2}, respectively). The PAM90 polymer adsorption by pyrophyllite was much greater than that adsorbed by Na-montmorillonite, despite the fact that the surface area of the latter was ~20 times

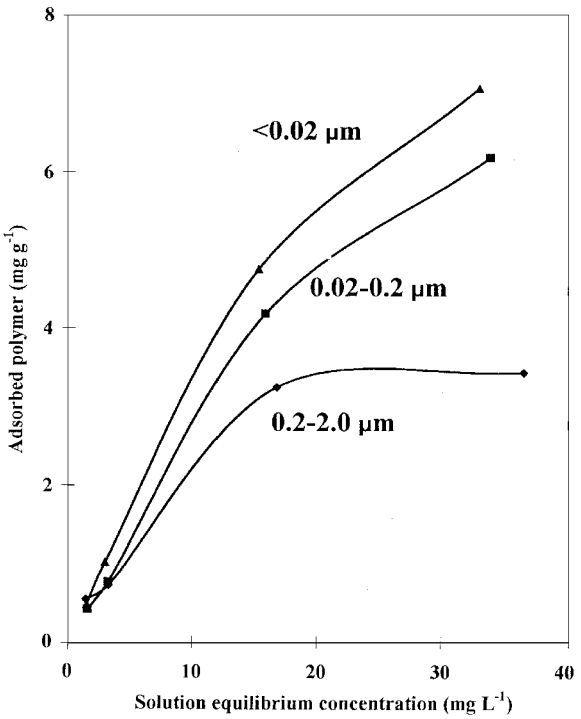


Figure 2. The effect of the particle size of pyrophyllite on the adsorption of PAM90 in clay suspension at a concentration of 1 g L^{-1}, at pH 7, in the absence of free electrolytes.

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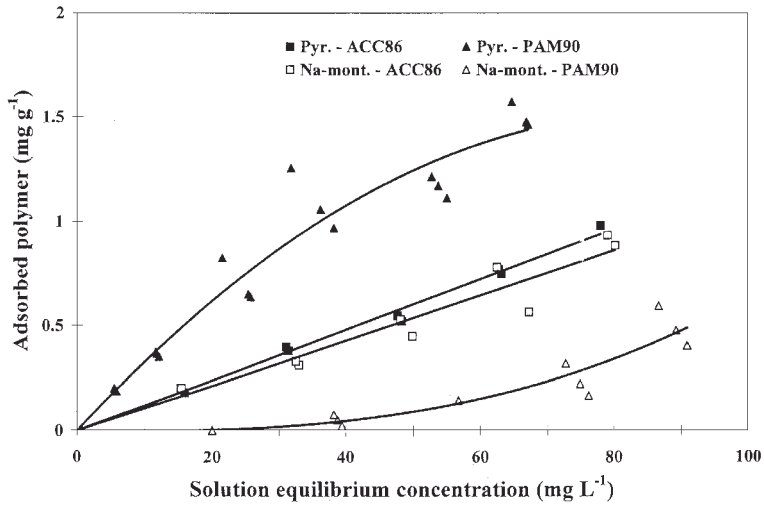


Figure 3. The effect of degree of hydrolysis of two anionic polyacrylamides on their adsorption by Na-montmorillonite and pyrophyllite in a clay suspension at a concentration of 22.5 g L^{-1}, at pH 7, in the absence of free electrolytes.

greater than that of the former. The PAM90 molecules were in their extended conformation, because of their high DH and the low electrolyte concentration in the suspension. The extended conformation resulted in strong repulsive forces, both intra-molecular and inter-molecular (Stutzmann and Siffert, 1977). Thus, the low level of PAM90 adsorption by Na-montmorillonite was probably due to the repulsive forces that develop between the negatively charged extended chain polymer molecules and the extended negative electric field, associated with the basal surfaces, around the Na-montmorillonite platelets. This negative electric field influences the edges, making them less accessible to approaching negatively charged PAM90 polymer molecules, to which it acts as a potential barrier. The absence of such a negative electric field around the pyrophyllite particles increased the accessibility of the adsorption sites to the negative PAM90 molecules, thus enhancing PAM adsorption. Under these conditions, however, a hydrophobic bonding mechanism is also possible for PAM90 adsorption on pyrophyllite (Laird, 1997).

Whereas pyrophyllite adsorbed much more PAM90 polymer than Na-montmorillonite under the same conditions, the isotherms for ACC86 polymer adsorption on Na-montmorillonite and pyrophyllite were nearly identical (Figure 3). Because there is a very weak electric field associated with the basal surfaces of pyrophyllite particles, it is more likely that the lower adsorption isotherm for ACC86 polymer than for PAM90 was due to the differences in the polymer structure. The ACC86 polymer, which has significantly fewer anionic functional groups than PAM90, has a random coil structure that occupies a larger volume than that occupied by the PAM90 molecule (Mortimer, 1991). The ACC86 tends to coil in solution with the charged carboxylate groups pointing outwards and the hydrophobic chains which point inwards. Because of this conformation, the opportunity for interaction between the ACC86 and the pyrophyllite uncharged surfaces is minimized. Therefore, it is more likely that the main adsorption sites are located on the edge surfaces. Once the coiled ACC86 molecules are adsorbed on the clay surface, they impede other molecules from approaching adjacent sites (Espinasse and Siffert, 1979). The number of functional groups exposed on the external surfaces of the coiled molecules, available to participate in their adsorption reactions, is smaller than the number available in the extended molecules, for a given amount of polymer. Since there is a very low basal electrostatic charge in pyrophyllite, the steric hindrance effect of adsorption sites on the edge surfaces could explain the smaller amount of ACC86 adsorbed by pyrophyllite. In contrast to pyrophyllite, the affinity of Na-montmorillonite for ACC86 polymer was greater than that for PAM90 (Figure 3). This was probably due to the presence of a negative electric field, associated with the basal surfaces, around the Na-montmorillonite particles. Thus, the repulsive forces between the negative electric field and the negatively charged PAM90 polymer were stronger than those acting for the ACC86 polymer.

CONCLUSIONS

The results of the present study have shown that the adsorbed polymer concentration increased as the pH decreased and the solution NaCl concentration increased. The adsorption of PAM90 polymer per unit weight of pyrophyllite increased as the particle size of the clay decreased and the adsorption of PAM90 polymer by pyrophyllite was much greater than that by Na-montmorillonite despite the fact that the surface area of Na-montmorillonite was ~20 times greater than that of pyrophyllite. The adsorption of PAM90 was greater for pyrophyllite than for Na-montmorillonite, but the

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affinity of both clays for ACC86 was about the same. Whereas the affinity of Na-montmorillonite for ACC86 was greater than for PAM90, the opposite was observed for pyrophyllite. These results were attributed to the repulsive forces which develop between the negatively charged, extended-chain polymer and the extended negative electric field associated with the basal surfaces, around the Na-montmorillonite platelets. This extended negative electric field may influence the edges, making the latter less accessible to approaching negatively charged polymers. The results suggest that the edge surfaces of the clay minerals may play a major role in PAM adsorption.

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