Adsorption Characteristics of Polyacrylamide and Sulfonate-Containing Polyacrylamide Copolymers on Sodium Kaolinite

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Synopsis

Polyacrylamide and its copolymer containing 6.8 mole % 2-acrylamido-2-methylpropane sulfonic acid were prepared by an irradiation-initiated precipitation polymerization technique. The polymer was characterized by intrinsic viscosity under conditions similar to those used during adsorption measurements. Hydrolytic degradation of the polyacrylamide was found to be negligible under conditions used. The adsorption substrate, sodium kaolinite, was prepared by extensive ion exchange treatment. Equilibrium adsorption of the polymers on the sodium kaolinite was made as a function of polymer concentration, solution pH, ionic strength, and temperature.

INTRODUCTION

High-molecular-weight polymers play a major role in water treatment,[1] flocculation of colloidal suspensions,[2,3] and mobility control in micellar-polymer flooding technology.[4,5] These applications have been the subject of recent reviews.[6–8] Polyacrylamide and its copolymers hold special importance because of their use in all of these areas. However, as mobility control agents in enhanced oil recovery techniques, the efficiency of polyacrylamide is reduced for two reasons. First, the polymer is degraded in the shear flow that is most severe at the points of injection into the well; second, the polymer is irreversibly retained within the porous structure of the reservoir material.[9,10] Its retention results from physical entrapment and chemical adsorption on the mineral surfaces. This report focuses on the problems of polymer adsorption.

Polymer interaction with solid surfaces is well documented in the literature.[11] The adsorption of highly charged polyelectrolytes such as poly(styrene sodium sulfonate) to latex particles has been studied.[12] The characteristics of the adsorption of poly(vinyl alcohol), a nonionic hydrophilic polymer, has been studied in relation to several different surfaces, for example, silver iodide,[13] aluminum oxide,[14] and silica.[15] Studies of the adsorption of polyacrylamide and its hydrolytic decomposition products have also been conducted for a large number of different substrates, including calcium carbonate,[16] china clay,[17] calcium phosphate,[18] cellulose,[19] and kaolinite.[20–24]

However, in most of these instances, the characterization of the surface or of the polymeric component is not always complete. In this report, we focus on the adsorption of polyacrylamide on well-characterized sodium kaolinite. Although the mineral in most oil reservoirs is like Berea sandstone, the adsorption

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of polymer in this strata is most often due to the presence of minor components, such as clay. Although present only in small amounts, the clay component comprises a large fraction of the exposed surface area within the reservoir. (Griffith[25] indicates that common Berea sandstone contains about 3–7% kaolinite, with minor amounts of montmorillonite and illite.) Thus, this work investigates the effects of ionic strength, pH, and polymer charge on the adsorption characteristics of polyacrylamide copolymers.

EXPERIMENTAL

Synthesis of Acrylamide Polymers

Acrylamide (Eastman, electrophoresis grade) and 2-acrylamido-2-methylpropane sulfonic acid (Lubrizol Chemicals, research grade) were obtained as crystalline powders and used without further purification. Acrylamide labeled in the 1-position with carbon 14 was obtained from New England Nuclear with a specific activity of 0.1995 millicurie per millimole. It was used also as a received.

Because of the difficulty of purifying polymer and radioactive monomer in a solution polymerization, the tagged polyacrylamide (PAM) and its copolymer with the sulfonated monomer (PAMS) were prepared following the procedure for a precipitation polymerization as described by Wada, Sekiya, and Machi.[26]

Acrylamide (19.9 g) and ^{14}C-labeled acrylamide (0.06 g) were dissolved in an acetone water solution (45/55, v/v) to yield a solution that was $2.5M$ in monomer. The solution was placed in a polymerization tube where nitrogen was bubbled for 30 min under conditions which did not alter the monomer or solvent composition. The reaction mixture was sealed and irradiated with a cobalt-60 irradiation source at a dose rate of 0.6 krad/hr for a total dose of 28.8 krad (48 hr). The polymer yield was 87%. The unreacted monomer was removed by repeated washing of the precipitate in a blender with acetone. The polymer was then freeze-dried to a fine white powder and stored at 4°C prior to use.

A similar procedure was followed in the preparation of the sulfonated copolymer. Acrylamide (15.94 g), tagged acrylamide (0.06 g), and the AMPS monomer, 2-acrylamide-2-methylpropane sulfonic acid (4 g), were dissolved in an acetone–water mixture (50/50, v/v) and polymerized for a similar period of time to give a 67% yield of polymer. The polymerizations were repeated for untagged materials with similar yields. All polymers were characterized by measuring their intrinsic viscosities in either water or NaCl solution at 30°. Elemental analysis indicated that the PAMS polymer was 6.8% AMPS, which agrees well with the overall starting composition (12% AMPS).

Intrinsic viscosities were measured at 30°C in a standard Ubbelhode viscometer. The data reported here were not corrected for the shear rate effect on the viscosity, which is expected to be small but significant for high-molecular-weight polymers such as those used in this work. In distilled water, the Mark–Houwink viscosity parameters for polyacrylamide are $K = 6.31 \times 10^3$ dl/g and $a = 0.8$ at 30°C.[27] Similar parameters are not available for the acrylamide copolymers.

Preparation of Sodium Kaolinite

Our starting material was a well-crystallized sample of Georgia kaolinite (from the University of Missouri repository), having a surface area of 9.82 m^2/g as determined by nitrogen adsorption. The dry clay was treated with water for 10 min in a high-speed mixer at a solid-to-liquid ratio of 0.5, then diluted with distilled water to 5% solids and allowed to settle. The kaolinite was repeatedly washed with intense agitation until there was no change in the conductivity of the supernatant water. A NaCl solution (2M) was added to the solids and agitated at a high solid-to-liquid ratio for 30 min, then diluted and agitated again for 2 hr, allowed to settle, and the supernatant decanted. The washing procedure was repeated until a pH 7 and a constant conductivity were observed in the supernatant. The kaolinite was repulped with 1M NaCl at pH 3, agitated for another 30 min, diluted with water, agitated for 2 hr, allowed to settle, and washed with distilled water to pH 7 and constant supernatant conductivity. The ion exchange procedure was repeated twice with the 1M NaCl, each time being followed with the same washing procedure. The final washings were with triple distilled water. The fine clay particles were then separated from the course ones by decantation. The fine particles were recovered and repeatedly washed with triple distilled water until the conductivity of the clay suspension became identical to that of the triple distilled water. The sodium kaolinite was allowed to settle, and the thick suspension was freeze-dried to yield a powder that was stored in a desiccator prior to use.

Adsorption Methods

Approximately 1 g of freeze-dried sodium kaolinite was weighed into a glass vial having a Teflon-lined screw cap. A 2000-ppm polymer solution in the appropriate electrolyte concentration was prepared. To the clay in the vial was added 2.5 ml of the supporting electrolyte (polymer free); this solution was kept at 30° with agitation for 2 hr. HCl or NaOH was then added to adjust the pH of the solution. After this conditioning step, a solution comprising a mixture of the polymer solution and a polymer-free solution having the same electrolyte concentration with the required polymer amount was added to the clay. The total liquid volume was 10 ml.

The adsorption time began at this point. The vial was agitated for a time in a constant-temperature incubator. At the end of the experiment, the sample was centrifuged at 1500 g for 20 min. A 1-ml sample of the supernatant was mixed with 13 ml Aquasol-2 liquid scintillation cocktail (dioxane-based, New England Nuclear) in a polyethylene scintillation vial. The sample was analyzed in an LS-100 C liquid scintillation system. This scintillation procedure could tolerate ionic strengths up to 3M. Using 1-ml samples of 10-ppm pure tagged polymer solutions in the absence of adsorption, the polyacrylamide polymer (PAM) gave 178 cpm and the copolymer containing the sulfonate, PAMS, gave 150 cpm.

When experiments were performed at 60°C, the procedure was slightly modified. The samples were equilibrated with the sodium kaolinite at 60° with shaking for 24 hr. The samples still at 60° were allowed to settle for a period of 24 hr. The supernatant was centrifuged in an insulated centrifuge tube for 10 min, during which time the temperature was observed to fall about 8° to 52°. A 1-ml aliquot of this solution was used for the scintillation measurement.

DISCUSSION OF RESULTS

Before considering the interaction between the polyacrylamides and the sodium kaolinite surface, it is necessary to describe the properties of each material as it exists alone in the experimental medium. The properties of both components are dependent on the nature of the medium, the ionic strength, pH, and temperature. Kaolinite is an aluminosilicate $[Al_4Si_4O_{10}(OH)_8]$ whose crystal structure contains alternate sheets of alumina and silica oxides. As the crystal units have planar habits, there are two principal surfaces: the edge containing exposed metal ions, and the oxide surfaces. Kaolinite exchanges cations and, in this work, the sodium form of the mineral was prepared. Buchanan and Oppenheim[28] investigated the stability of kaolinite in aqueous suspensions. With pH < 4, the aluminum cations may be dissolved from the lattice; in the pH range 4–9, a $Si(OH)_4$ entity in some form is leeched away; and at higher pH values, the aluminate ions become freed.

In our preparation of sodium kaolinite, care was taken to maintain the clay during the washing and conditioning steps between pH 4.5 and 7 in order to minimize the leeching of aluminum ions from the crystal matrix. However, despite carefully controlled conditioning steps, kaolinite is unstable in electrolyte solutions such as those used in the adsorption experiments here considered. As determined by Williams and Williams[29] and by Hunter and Alexander[30] from electrophoretic mobility measurements, the surface charge of kaolinite is a function of solution pH and solution ionic strength. At high pH, the surface is negatively charged; the magnitude of the charge drops slightly as the ionic strength is increased from 10^{-4} to 10^{-2} molar NaCl. At pH 5, the surface charge, still negative, is nearly independent of the electrolyte ionic strength. At pH 3, the surface is slightly negatively charged in the presence of electrolyte, but becomes positive at very dilute electrolyte concentrations. The positive charge is attributed to the metal ions on the edges of the kaolinite crystal lamellae. Although heterogeneous surface charge is indicated from crystal structure considerations, in this work we will interpret the results solely in terms of the overall kaolinite surface charge. No measurements have been made in this work on the electrophoretic mobility of sodium kaolinite to which polymer is adsorbed.

Polymerization was carried out with initiation by γ-irradiation in a medium free of all components but the monomers and solvent system. The polymers so produced were free from impurities which might alter their interactions with adsorbing surfaces. At the low doses used, no significant branching occurs during the radiation-induced synthesis. A combination of chain scission and chain branching is expected in side reactions at much higher levels.[31] Although the reactivity ratios for this copolymerization are not known, they may be reasonably approximated by those for acrylamide ($r_1 = 1.1$) and sodium acrylate ($r_2 = 0.3$), as reported by Plochocka and Wojnarowski.[33] The ideal copolymer equation predicts that the initial copolymer composition from a 12 mole % AMPS monomer mixture in acrylamide would be 10% AMPS, and that the composition of copolymer being produced at 60% conversion would be about 13%. Although the analyzed composition of 6.8% AMPS is somewhat lower, it nevertheless is consistent with the predictions of the copolymer equation. Because of the economics of making ^{14}C-labeled materials, these copolymerizations were taken to a high conversion. The application of the ideal copolymer equation is not strictly correct, since precipitation occurs during the growth of the polymer chain.

In order to interpret the adsorption results for the copolymer, we will assume homogeneous polymer composition and molecular weight.

Two polyacrylamide polymers were used in the adsorption studies—a homopolymer PAM and a copolymer PAMS contained 6.8% of the AMPS. The PAM was prepared as an uncharged polymer without any significant degree of hydrolysis of the pendent amide groups to carboxylic acid form. The intrinsic viscosity of PAM determined at 30° [Fig. 1(a)] is independent of the ionic strength of the solution in which the viscosities were determined. This intrinsic viscosity is a measure of the effective hydrodynamic volume of the polymer coil in solution.[34] For the PAM in these experiments, the expansion of the coil is independent of the electrolyte concentration. However, the PAMS containing 6.8 mole % of monomer with a strongly ionic sulfonate group have an intrinsic viscosity that increases sharply as the ionic strength of the solution decreases to 10^{-2} molar NaCl [Fig. 1(a)]. Coulombic repulsion along the polymer chain becomes more significant at low concentrations of supporting electrolyte.[35,36] This electrostatic repulsion causes an expansion of the polymer coil and an increase in its effective hydrodynamic volume in solution. In contrast to the PAM, the PAMS is expected to exclude coions from the domain of the polymer coil in a Donnan-like manner at low ionic strengths of the supporting electrolyte.

Figure 1(b) shows the effect of pH on the intrinsic viscosity of PAM, PAMS, and a copolymer of acrylamide and acrylic acid having approximately the same composition as the PAMS. The intrinsic viscosity of PAM at both low and high ionic strength is independent of the solution pH. The PAMS has a significantly higher intrinsic viscosity which passes through a shallow maximum at pH 6. The sulfonate polymer, while exchanging its counterions readily as the pH changes, is much less sensitive to pH than is the corresponding carboxylate-containing copolymer. The weakly acidic carboxylate-containing copolymer has an intrinsic viscosity at low pH which approaches that of the PAM. Most of the carboxylate groups are in the associated hydrogen form. However, at high pH, as they ionize with the sodium counterion, the polymer coil is expanded and the intrinsic viscosity approaches that of the PAMS. The ionization of the PAMS is believed to be independent of pH.

Since the adsorption experiments extended over long periods of time, it was necessary to consider the possibility that the polymers used in this work had decomposed under experimental conditions. Palit and co-workers[37] have presented data which indicate rapid hydrolysis of PAM in strongly alkaline solutions. Under milder conditions, Shyluk and Stow[38] have shown that PAM undergoes an aging which results in a drop in solution viscosity. In Figure 2, the relative specific viscosities are given for a 2000-ppm PAM solution as a function of equilibration time at the indicated conditions. Equilibrium adsorption measurements normally required 72 hr of contact with the kaolinite suspension. At both 30 and 60°C, PAM retained its viscosity near its initial value. Over longer times at 60°, an increase in viscosity was observed when measured in a solution of zero ionic strength. At the same equilibration conditions (save for being in 1 molar in NaCl), the PAM retained a more constant relative viscosity. Hydrolysis is indicated. In the absence of NaCl, the polyelectrolyte effect causes an increase in viscosity. In salt, this expansion of the coil is not observed. This constant viscosity, however, indicates that no chain scission occurs during the equilibration time. Under conditions of high pH and long equilibration times,
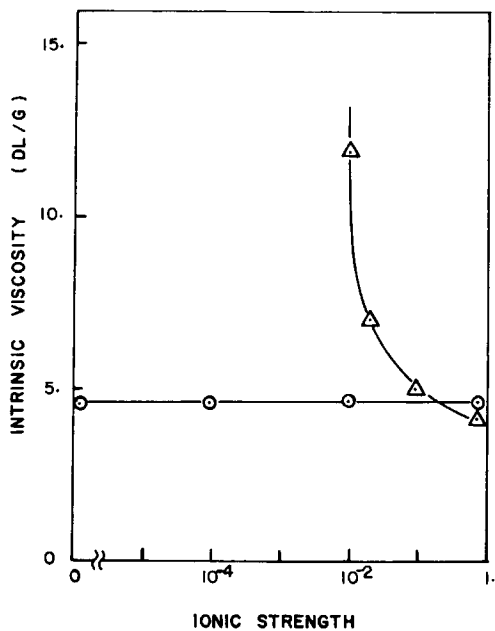
(a)
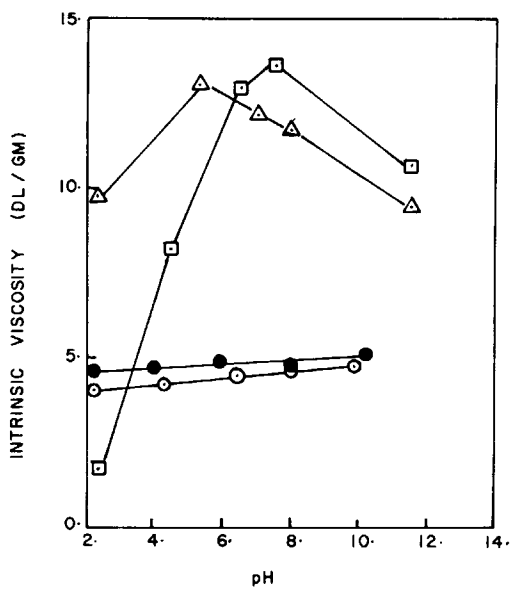
(b)

Fig. 1. (a) Intrinsic viscosity of polyacrylamide and the copolymer PAMS as a function of ionic strength. Electrolyte NaCl; temperature 30°C: (⊙) PAM; (▲) PAMS. (b) Effect of solution pH on the intrinsic viscosity of polyacrylamide and its copolymers. Temperature 30°C: (△) PAMS in 10^{-2} M NaCl; (▫) PAMC in 10^{-2} M NaCl; (●) PAM in 1M NaCl; (⊙) PAM in distilled water.
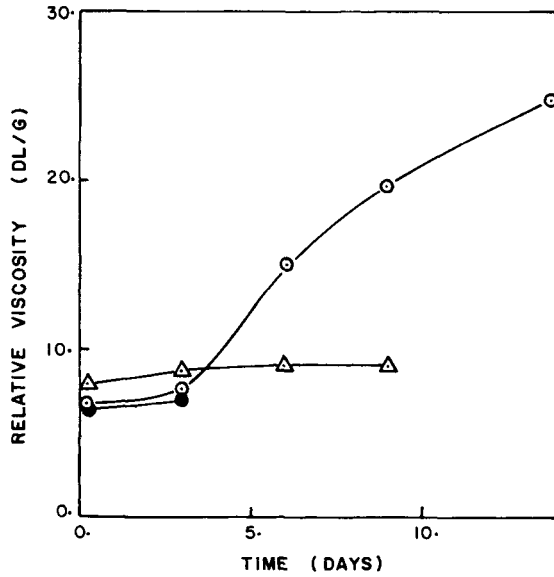
Fig. 2. Relative viscosity of a 2000 ppm PAM solution as a function of equilibration time without agitation: (⊙) in distilled water at 60°C; (●) at 30°C; (▲) in 1M NaCl at 60°C.

it was sometimes observed that the amount of polymer adsorbed slowly decreased over time.[42] This decline may be attributed to the effects of hydrolysis and of the hydrolysis products on the adsorption equilibrium.

In Figure 3, the amount of PAM adsorbed on sodium kaolinite is plotted as a function of time for experiments performed at 30°. The ionic strength (I) refers to concentration of NaCl in ppm. In all but one of the experiments, the solid-to-liquid ratio (S) was 0.1. The amount adsorbed (mg/g) was less when the solid-to-liquid ratio was high for a given initial polymer concentration. All other conditions being the same, the final equilibrium polymer concentration was lower for higher solid-to-liquid ratio. The reported pH represents the final hydrogen
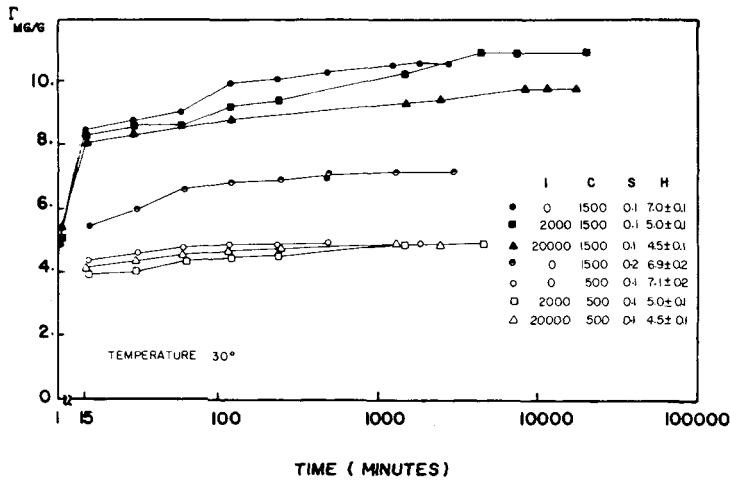

Fig. 3. Kinetics of PAM adsorption on sodium kaolinite at the conditions indicated. I is concentration of NaCl in ppm; C is the initial PAM concentration in ppm; S is the solid-to-liquid ratio, and H is the initial solution pH.

concentration which resulted from the adsorption process, as in Fig. 3 no adjustment was made in the solution pH. The rate of adsorption of PAM on sodium kaolinite was rapid—approximately 80% occurring within the initial 15 min of contact time. An adsorption plateau was established after 100 min and was maintained with only a slight drift over a long period of time. The rate of adsorption was independent of initial conditions.

During these adsorption experiments, the concentration of polymer in solution dropped to a low value. The analysis by Jankovics[18] for the kinetics of a Langmurian adsorption was not applied to these data because the adsorption was too rapid. Although data at very short times are most useful for determining the adsorption kinetic parameters, they were not obtained. To ensure full equilibration of the surface with the components in solution, equilibration times of 72 hr (4320 min) were used in adsorption experiments performed at 30° with both PAM and PAMS.

In Figures 4(a)–(e), adsorption isotherms at 30° for PAM on sodium kaolinite are plotted as a function of the equilibrium polymer concentration. Isotherms are given for adsorption at natural pH (resulting when no HCl or NaOH is added to the system) and for higher and lower pH values (resulting from addition of acid or base to the kaolinite during the conditioning step). The pH did not shift more than 0.2 pH units during the course of a typical absorption experiment; all of the reported pH data refer to the final equilibrium pH of the solutions.

The adsorption studies were performed in a supporting electrolyte, NaCl, which varied in concentration from 0 (for distilled water) to $3M$. In solutions of high ionic strength [Fig. 4(a)], the adsorption isotherm shifts to lower absolute adsorptions as the solution pH increases. At low ionic strengths, the decrease in adsorption that accompanies a change in pH from 2.2 to 7.2 is small. A very significant drop occurs in the high pH ranges. Under these experimental conditions, the essentially nonionic PAM does not significantly change its equilibrium shape in free solution. This is confirmed by the intrinsic viscosity data for PAM in these same polymer solutions. Michaels and Morelos[23] have reasoned that the interactions between PAM and surfaces such as kaolinite result from hydrogen bonding between the amide hydrogen atoms and the oxygen groups on the aluminosilicate surface. In the absence of any significant charging effect on the PAM, this surface interaction results in a very favorable partitioning of the polymer from its condition in free solution to an aggregation in a domain next to the mineral–water interface. The pH effect observed results from the changes in the surface character of the kaolinite. Between pH 2 and 7, the kaolinite has a surface charge which changes from a slightly positive to a moderately negative value.[29] Under these conditions, there is only a slight shift in the adsorption of the PAM, implying only a slight alteration of the interaction between the kaolinite and the PAM.

However, when the surface charge on the kaolinite reaches highly negative magnitudes, the basic attractive interaction of the uncharged PAM with the kaolinite surface is weakened. The kaolinite–PAM interaction is reduced in the strongly ionic domain of the interface at high pH conditions. The slight drop in PAM adsorption, as the ionic strength is increased at constant pH, is also consistent with this. The natural pH of adsorption of PAM on sodium kaolinite is a function of solution ionic strength. In Figure 4(a), ionic strength $3M$ NaCl, the natural pH is 4.4. As the ionic strength is reduced to zero [Fig. 4(e)], the

FINAL POLYMER CONCENTRATION (PPM)

(a)

FINAL POLYMER CONCENTRATION (PPM)
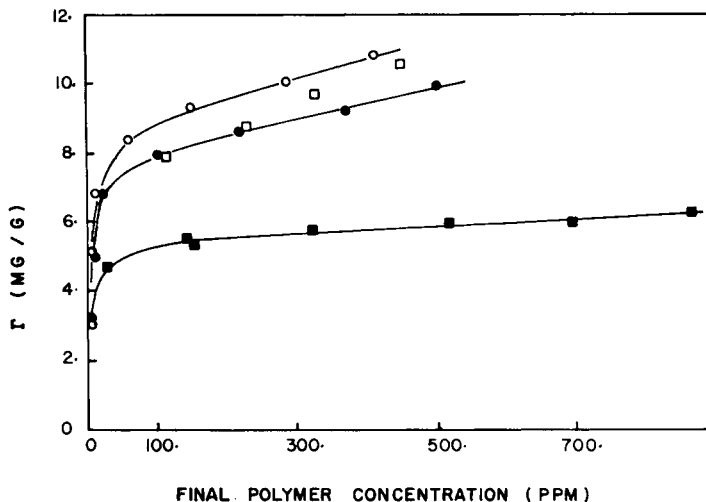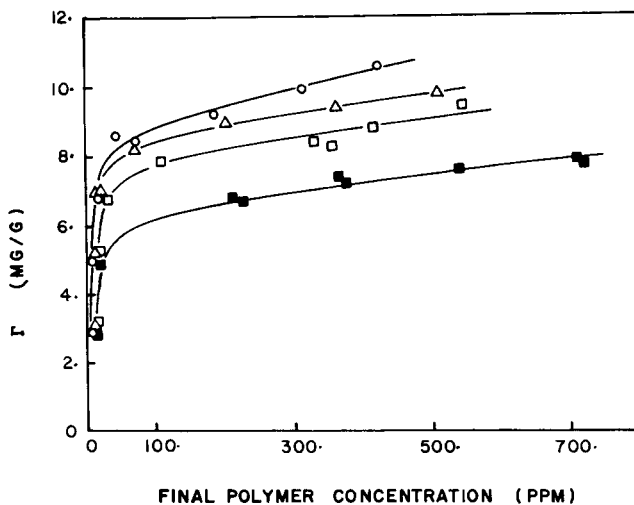
(b)

Fig. 4. Equilibrium adsorption of PAM on sodium kaolinite as function of final polymer concentration.   Temperature 30°C; S is 0.1; equilibrium time 72 hr; indicated pH is final equilibrium value.   (a) Ionic strength $3M$ NaCl: (O) pH 1.6; (□) pH 4.4 (natural); (●) pH 6.7; (■) pH 11.3.   (b) Ionic strength $1M$ NaCl: (O) pH 2.0; (△) pH 4.5 (natural); (□) pH 6.6; (■) pH 10.3.   (c) Ionic strength $0.1M$ NaCl: (O) pH 2.3; (△) pH 4.7 (natural); (□) pH 7.4; (■) pH 11.9.   (d) Ionic strength $10^{-2}M$ NaCl: (O) pH 2.2; (△) pH 5.4 (natural); (□) pH 7.2; (■) pH 10.9.   (e) Distilled water: (O) pH 2.3; (□) pH 6.9 (natural); (▲) pH 10.8.

natural pH shifts to 6.9.   At high electrolyte concentration, there is an exchange of the hydrogen ions of the clay with the sodium ions in the water resulting in a lower pH.

In most cases, the adsorption increased sharply as the equilibrium solution polymer concentration increased to 100 ppm.   The isotherms did not, however, level off to a plateau of constant polymer adsorption but slowly increased as the polymer in solution rose to 500 ppm.   For PAM, only at the very high values could
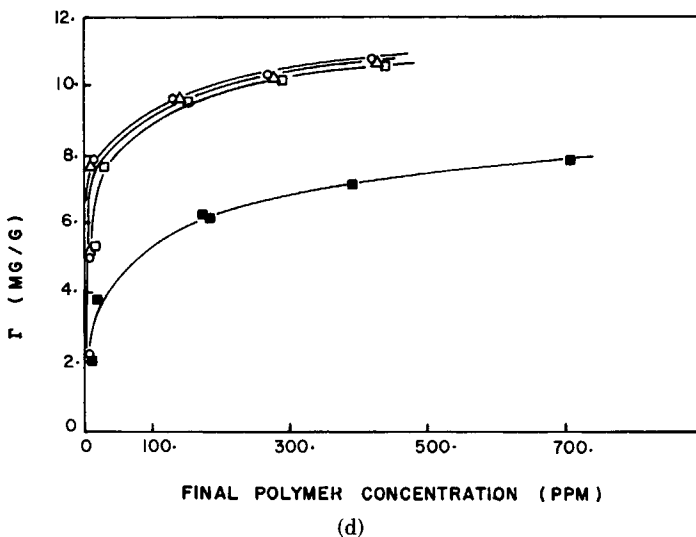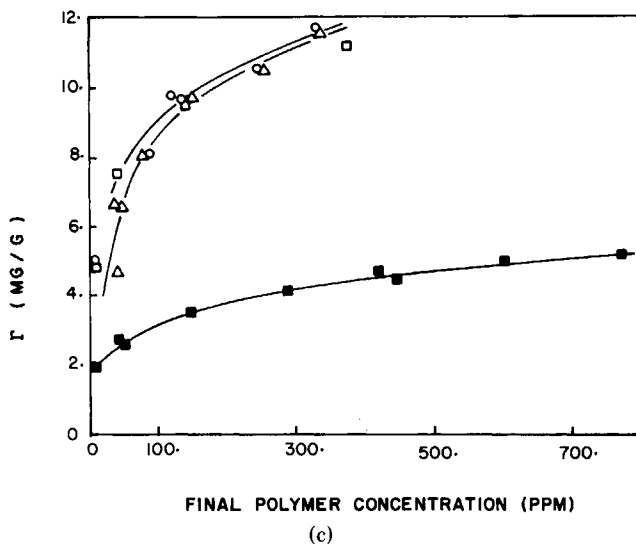
(c)

(d)

Fig. 4. (*Continued from previous page.*)

a definite plateau limit in the adsorption be observed. Using the standard correlation, these adsorption data did follow a Langmurian pattern. No evidence of a multilayer adsorption of the PAM was encountered. Adsorption isotherm shape for the PAM indicates no significant cooperative interaction between the PAM on the interface and those about to be adsorbed from the solution. The PAM molecules on the surface occupy lattice spaces independently of the other polymer molecules already on the surface.

In Figures 5(a) and (b), the equilibrium adsorption isotherms are given for the ionic PAMS polymer as a function of polymer concentration, solution ionic strength, and pH. Although the shape of the adsorption isotherms is similar to those of the PAM, two important differences should be noticed as polymer concentration is increased. For a given ionic strength in the supporting elec-

FINAL   POLYMER   CONCENTRATION   (PPM)
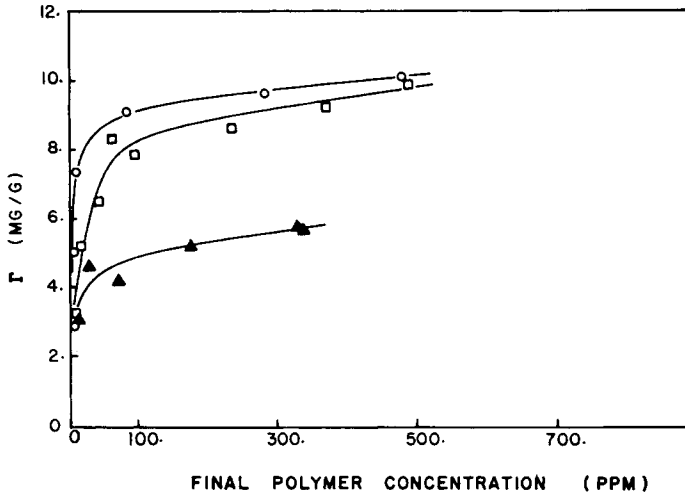
(e)

Fig. 4. (*Continued from previous page.*)

trolyte, the adsorption drops off in a regular manner as the pH is increased from 2 to 9.   This reflects the increase in Coulombic repulsion as the surface charge on the kaolinite becomes more negative in the regions of high pH.   The ionic character of the PAMS backbone does not change substantially as the pH is changed in this region.

In addition to the pH effect, there is a very strong ionic strength effect on the absolute amount of polymer adsorbed.   At low ionic strengths, the adsorption is near zero as the electrostatic repulsion between polymer and surface is high. As the ionic strength is increased, the supporting electrolyte suppresses the extent to which the fixed charges on the polymer and surface can dominate the inter- actions.   In a 1 molar solution, although the effect of pH is still observed, the absolute adsorption of the PAMS is in the same range as that observed for the uncharged PAM.

Figure 6 summarizes the adsorption characteristics of the two polymers on sodium kaolinite at an equilibrium polymer concentration of 100 ppm.   Unlike the PAM, the PAMS has an adsorption which is suppressed under conditions of low ionic strength in the supporting electrolyte.   The absolute adsorption of the PAMS increases at high ionic strengths into a region comparable (although still lower) to the PAM.   The effect of ionic strength on the adsorption of the PAMS follows a commonly encountered pattern for electrostatic rejection of a charged body from a similarly charged polyelectrolyte.

It was difficult to measure the adsorption of these polymers at elevated tem- peratures because a room temperature centrifuge had to be used.   With proper insulation of the centrifuge tube, a temperature drop of less than 8°C was en- countered.   The data in Figures 7(a) and (b) refer to experiments that were performed at 30 and 60° as a function of polymer solution concentration and ionic strength at natural pH.   The solutions were equilibrated at 60° for 24 hr, allowed to settle for another 24 hr, and the supernatant was centrifuged under conditions where the final solution temperature after centrifugation was about 52°.   This change in the temperature has an insignificant effect on the observed equilibrium isotherms.   There is no observed change in the adsorption of PAMS as a function
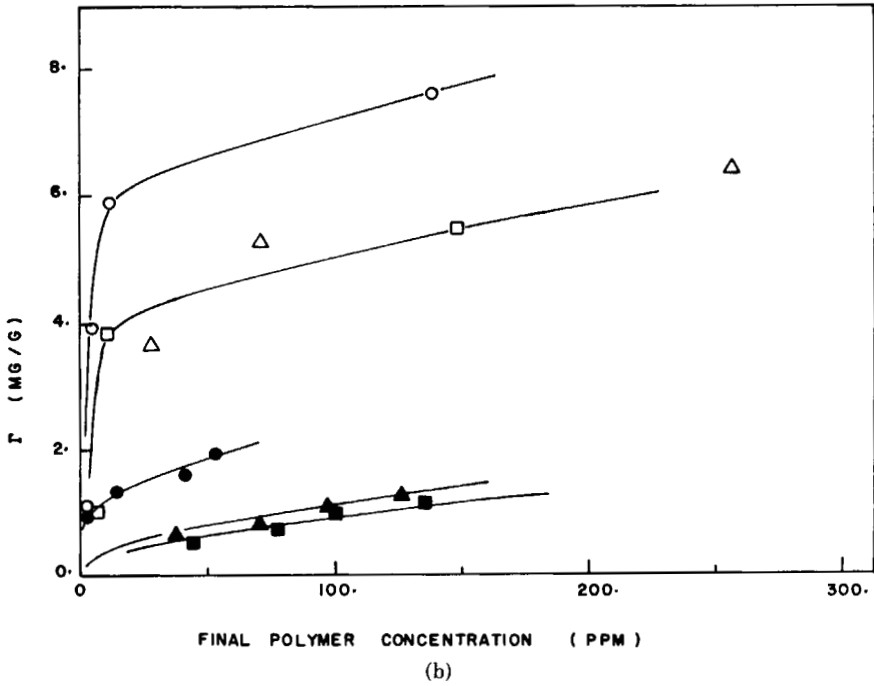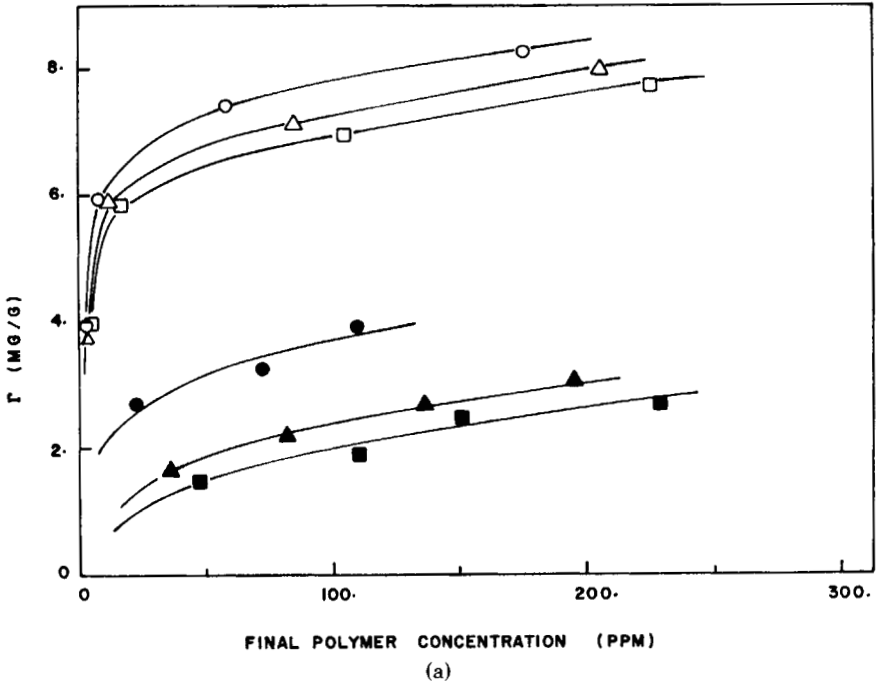
(a)

(b)

Fig. 5. Equilibrium adsorption of PAMS on sodium kaolinite as function of final solution polymer concentration (conditions as in Fig. 4).   (a) In $1M$ NaCl: (O) pH 3.8; (△) pH 6.5; (□) pH 8.7.   In $10^{-2}M$ NaCl: (●) pH 4.9; (▲) pH 7.5; (■) pH 9.4.   (b) In $10^{-1}M$ NaCl: (O) pH 2.5; (△) pH 4.4; (□) pH 7.7.   In $10^{-4}M$ NaCl: (●) pH 5.0; (▲) pH 7.7; (■) pH 10.0.
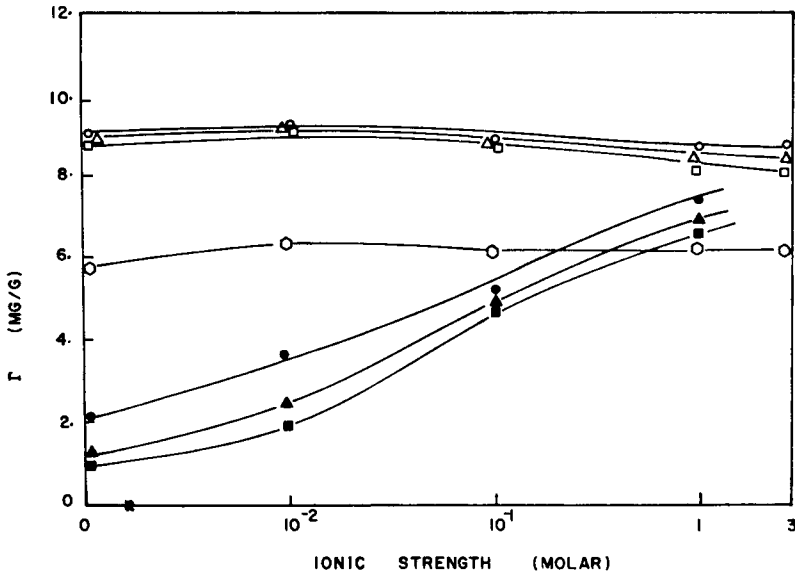
Fig. 6. Equilibrium adsorption of acrylamide copolymers as a function of ionic strength (final polymer concentration 100 ppm; other conditions as in Fig. 4).   PAM: (O) pH 2.5; (△) pH 5.0; (□) pH 7.0; (O) pH 10.5.   PAMS: (●) pH 5.0; (▲) pH 7.0; (■) pH 8.5.

of temperature for solutions of different ionic strength, even in the regions of high ionic strength, where much of the Donnan repulsion is suppressed.   The Coulombic effects still dominate the adsorption in a manner where temperature does not change the isotherm.

In Figure 7(b), similar data are given for the uncharged PAM.   For both conditions of low and high ionic strength, the adsorption isotherm is lowered as the temperature is increased from 30° to 60°.   Significant hydrolysis of the PAM under these conditions is doubted because of the data given in Figure 2, and because a hydrolyzed PAM being ionic should give a temperature effect analogous to the PAMS.   This reduction in the adsorption isotherm for the uncharged polymer is consistent with the hypothesis that a form of hydrogen bonding is responsible for the attraction of the PAM to the sodium kaolinite.   Such inter-actions are exothermic and thus are expected to weaken as the temperature is increased.

Adsorption of flexible-chain polymers such as polyacrylamide is rapid, and, in most reports, the reverse desorption under normal conditions is very slow.   At moderate pH, this adsorption is independent of ionic strength of the solution. This suggests a form of hydrogen bonding as the basis of the interaction between polymer and surface.   However, it is generally believed that a randomly coiled polymer such as polyacrylamide, if associated with a surface, cannot have a sig-nificant fraction of its chains attachments to the surface without a resulting very large decrease in configurational entropy.   Silberberg[39] has presented a picture of chain segments attached at specific points along the chain with long loops of polymer in a more or less random conformation extending out into solution. However, with polyacrylamides there is no reason to suspect that any one site on the polymer chain has any more preference for the surface than any other one. Given the kinetic turmoil that exists within a random coil as it moves through
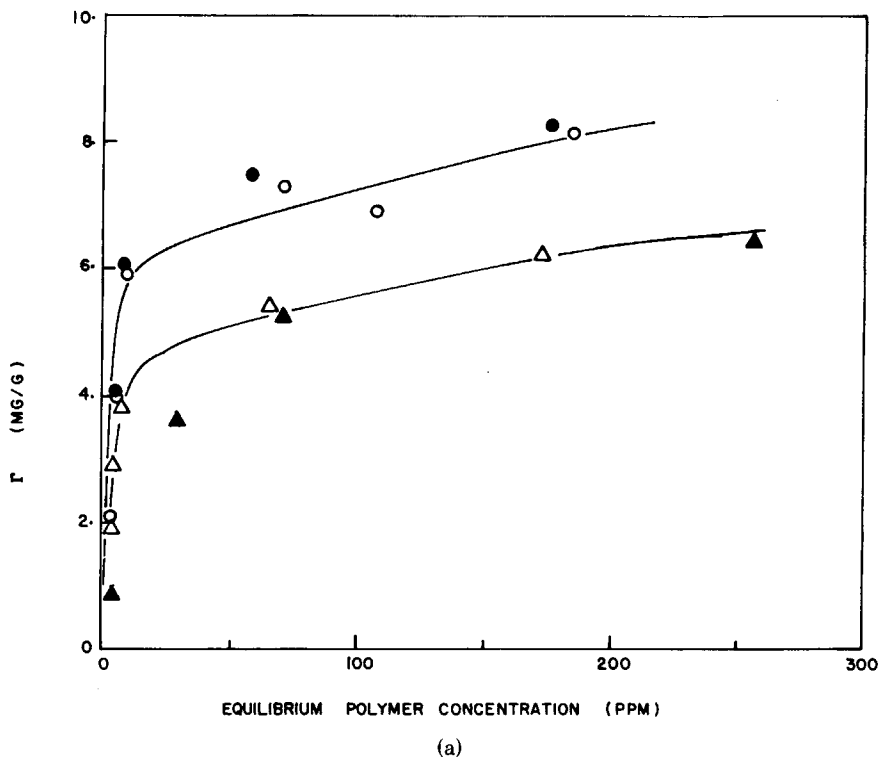
Fig. 7. Effect of temperature on the adsorption of acrylamide copolymers on sodium kaolinite. (a) PAMS: In $1M$ NaCl—(o) 60°C, pH 4.0; (●) 30°C, pH 3.8. In $0.1M$ NaCl—(△) 60°C, pH 4.4; (▲) 30°C, pH 4.4. (b) PAM: In $1M$ NaCl—(o) 60°C, pH 4.2; (●) 30°C, pH 4.5. In $0.1M$ NaCl—(△) 60°C, pH 3.7; (▲) 30°C, pH 4.7.

its ensemble of conformation shapes, it is reasonable to suspect that the interactions with the surface are transient. The hydrogen bonding at different sites is being continually made and broken, although on the average maintaining a certain number of interactions with the surface.

The interaction between the oxygens of the surface and the acrylamide may be analogous to the interactions that occur in solution between the oxygens of poly(oxyethylene) and the carboxylic acid hydrogens of unionized poly(acrylic acid).[40] These polymers form a coacervate in aqueous solution. The interaction energy between the ether oxygens and low-molecular-weight carboxylic acid groups has ebeen found from melting point depression measurements to be about 6 cal/cm^3 and exothermic.[41] As with PAMS, a change in the ionic character of the poly(acrylic acid) leads to a weakening of the association between the two components.

Desorption of polymers from such a surface is expected to be slow, as it is highly unlikely that all of the points of interaction of the polymer and surface will be simultaneously broken. For high-molecular-weight polymers in which there are on average a great number of interactions with the sites on the surface, total desorption of the molecule is impossible. This does not mean that the polymer molecule cannot move over the surface as the coverage of the surface increases. Surface diffusion envisioned as a rolling of the random polymer coil over the surface can easily occur without any need for total desorption of the polymer coil from the surface.
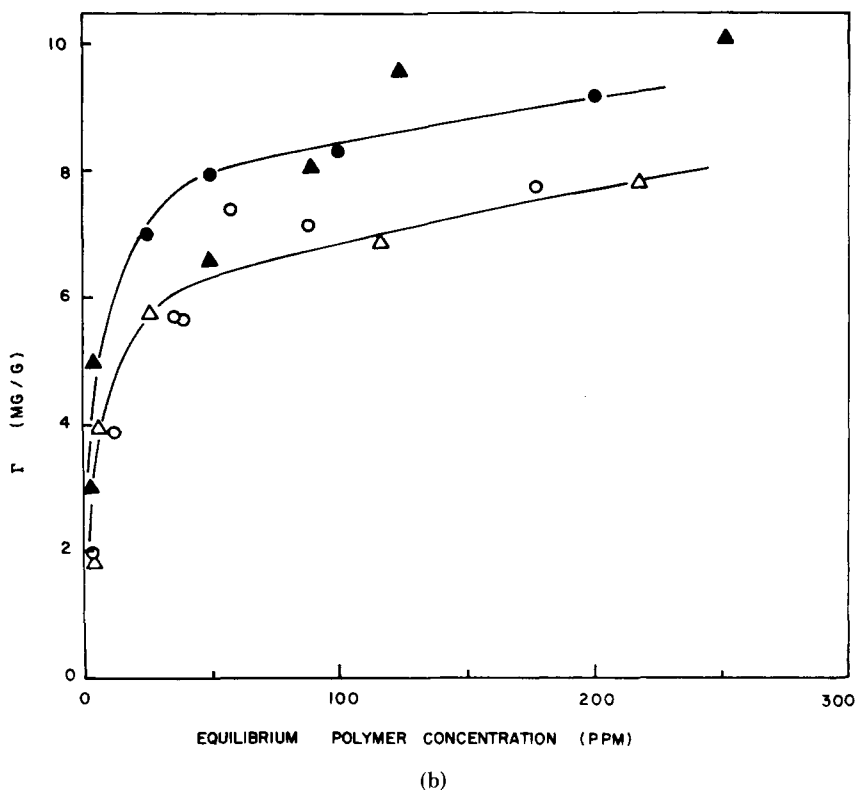
Fig. 7. (*Continued from previous page.*)

The effects of charge on the polymer–surface interaction may be viewed as a secondary interaction between the components whose effect is superimposed. The negative surface charge and the negative polymer fixed charge causes a reduction in the ability of the amide groups to hydrogen bond with the surface.

The electrostatic repulsions keep more of the chain elements of the coil away from the surface, particularly at conditions of low ionic strength. This makes it more difficult for polymer-surface hydrogen bonds to form. The result is a reduction in the effective adsorption at a given polymer concentration. As the supporting electrolyte concentration is increased, the Debye layer is suppressed, the polymer can approach the surface more closely, and the amide groups along the PAMS chain can once again form a complement of bonds with the surface. The absolute adsorption of the PAMS to the surface is reduced somewhat from that of the PAM at conditions of high ionic strengths because this polymer contains 6.8% by mole of a nonhydrogen bonding monomer in its backbone.

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