Desorption of Polyacrylamide and Hydrolized Polyacrylamide from Kaolinite Surface

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Desorption of labeled nonionic and hydrolyzed polyacrylamide from kaolinite in NaCl solutions is obtained using sodium metaphosphate as well as unlabeled polyacrylamide, whereas mere dilution with NaCl solution produced no measurable desorption. Extent of desorption achieved depends upon the charge characteristics of the polymer and the additives. Most interesting, desorption is found to depend upon the amount of original adsorption. Thus almost no polymer was desorbed at low surface coverages whereas up to 56% of a polyacrylamide polyacrylic acid could be desorbed at saturation surface coverage using sodium tripolyphosphate. Sodium metaphosphate desorbed less of the hydrolyzed polymer than the tripolyphosphate but both phosphates performed on an equal basis in the case of nonionic polyacrylamide. Results are discussed in terms of the configuration of the adsorbed polymer, detachment of individual segments of a polymer molecule from the mineral surface, and competition by the additives for the vacated sites and the contribution of the anionic species of the additives to the electrostatic repulsion between similarly charged polymers and mineral surface.

INTRODUCTION

Polymer performance in interfacial processes such as flocculation depends to a large degree on the nature and extent of its adsorption on particulate surfaces. While the amount of adsorption will depend on the initial levels of factors such as polymer concentration, pH, ionic strength, and temperature (1–6), perturbations in these levels are not known to cause any significant desorption.

Even though polymer adsorption has in general been considered to be irreversible in nature, the desorption properties of polymers have not been studied in detail. The apparent irreversibility of the polymer can be considered to result from the fact that the polymer may attach itself to the mineral surface at several separate points along its chain and not be able to desorb simultaneously from all sites before one or more of the detached segments re-adsorb. It should however be possible to desorb the entire polymer if vacated sites could be immediately blocked out by a competing agent as and when segments of the polymer molecule detach from the surface sites. This possibility was tested in this work using phosphates as competing agents for sites on a clay surface since they are known to have a strong affinity for clay minerals (7).

Desorption by dilution as well as by competing polymers was also investigated for comparison purposes.

EXPERIMENTAL

Kaolinite. Homoionic Na-kaolinite was prepared from a well-crystallized sample of Georgia kaolinite (KGa-1) obtained from the clay repository at the University of Missouri. The details of the procedure for the preparation of Na-kaolinite are given in Ref. (2). The surface area, determined by the nitrogen adsorption technique, was 9.4 m^2/g.

Kaolinite, $Al_4Si_4O_{10}(OH)_8$, has a two-layer crystal structure made up of a tetrahedrally arranged silica sheet and an octahedrally arranged alumina sheet. The cation-exchange capacity of kaolinite is quite low, amounting to 1–10 meq per 100 g. While the flat face is

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always negatively charged, the edges can be either positively or negatively charged depending on the pH.

Polyacrylamide and hydrolyzed polyacrylamide. The ^{14}C-labeled nonionic polyacrylamide (PAM), 9% hydrolyzed polyacrylamide (HPAM 9), and 33% hydrolyzed polyacrylamide (HPAM 33) used here were synthesized and characterized by American Cyanamid Company. The initial molecular weights of these polymers were reported to be 6.6×10^{-5}; however, some degradation was noted after more than a year of storage. This observed degradation resulted in a lowering of the molecular weights to 5.0×10^{-5} but was sufficiently slow as to not affect the current experiments.

Phosphates. The phosphates used, sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium metaphosphate ($(NaPO_3)_{13}$) were of analytical grade. Fresh phosphate solutions were prepared for each experiment.

Experimental procedure. For adsorption tests the clay (0.4 g) was first equilibrated for 2 hr in a 3×10^{-2} kmole/m^3 NaCl solution. A known volume of the polymer solution was then introduced, the pH and the ionic strength were adjusted to the desired values and the system agitated for 48 hr in order to reach equilibrium adsorption. The desorption tests were then conducted by recovering half of the supernatant for polymer concentration analysis and replacing it with 0.1 kmole/m^3 phosphate solution or NaCl salt solution with an adjusted pH to match that of the supernatant. The samples were next agitated for 96 hr after which the supernatant was again analyzed.

The polymer concentration of the supernatants was determined by measuring the residual ^{14}C-labeled polyacrylamide using a liquid scintillation counter.

RESULTS AND DISCUSSION

Adsorption Kinetics

The time required for reaching equilibrium was first determined by conducting tests as a function of agitation time. Results of these tests show that the kinetics of polyacrylamide adsorption on Na-kaolinite is rapid and the system attains equilibrium in about 24 hr (8). The initial rapid adsorption indicates that PAM has strong affinity for the clay surface. To assure equilibrium during all tests, 48 hr was chosen as the agitation time for the present study.

Adsorption Isotherms

The adsorption isotherms for PAM, 9% hydrolyzed PAM and 33% hydrolyzed PAM are given in Fig. 1. All the three isotherms exhibit a sharp rising region followed by a slow rising/plateau region. Analysis of the residual polymer in solution showed that at low concentrations, up to about 200 mg/kg polymer addition for PAM and 100 mg/kg polymer addition for the hydrolyzed PAM, all the polymer added to the system was removed from solution by adsorption onto the clay surface. At higher concentrations, however, adsorption does not continue to occur in the same manner. The observed increase in adsorption in this region could result from a crowding effect which pushes additional polymer into contact with the clay, owing to possible rearrangement of the adsorbed polymer from that of "flat" coverage to one of "point" adsorption with segments of polymeric chains extending into solution or from adsorption on lower energy sites.

The effect of polymer charge density is clearly seen in the above data. As the charge density is increased, the overall adsorption is found to decrease. This is to be expected for an anionic polymer since the clay surface is negatively charged. Adsorption of polymers on mineral surfaces is considered to occur due to hydrogen bonding aided by electrostatic and covalent bonding in the case of polymers with appropriate functional groups. While hydrogen bonding is mainly responsible for the adsorption of the nonionic polyacrylamides, electrostatic forces can be expected to play a measurable role for that of the hydrolyzed polyacrylamide owing to the presence of the

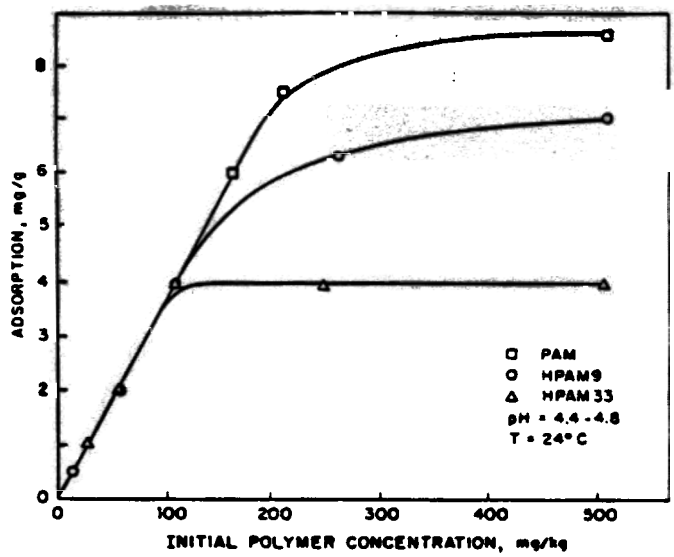

FIG. 1. Adsorption isotherms of polyacrylamide and hydrolyzed polyacrylamides on Na-kaolinite in 3 × 10^{-2} kmole/m^3 NaCl.

anionic (−COO) functional groups. Covalent bonding between active groups of the polymer and cations of the minerals has also been considered for a polyacrylamide/kaolinite system (7). In the present case, as the degree of anionicity of the polymer is increased, the adsorption decreases due to increased overall electrostatic repulsion between the clay and the polymer and that among the polymer in the adsorbed layer. The degree of anionicity of the polymers does not, of course, have an effect on the equilibrium adsorption density at low polymer concentrations where all the polymer is depleted from solution (Fig. 1). The latter is also indicative of the fact that the effect of anionicity of the polymer is felt more strongly in the "polymer crowding" region rather than in the high affinity adsorption region.

Desorption

First, the result of simple dilution was determined by removing half of the supernatant and adding an equal volume of NaCl solution adjusted to the desired pH and ionic strength. This was found to produce no detectable desorption of the polyacrylamide (see Figs. 2a and 2b). There was no effect of NaCl even when its level was increased to 0.5 kmole/m^3.

As phosphates are known to exhibit special complexing properties with many reagents, the effect of sodium tripolyphosphate and sodium metaphosphate was next investigated. Percentage desorption of the polymers expressed in terms of

$$\frac{\text{Amount of adsorbed polymer removed from the clay surface}}{\text{Amount of total polymer adsorbed initially}} \times 100$$

is given in Figs. 3a and b as a function of residual and initial polymer concentration, respectively. It is seen that as much as 56% of the adsorbed polymer could be desorbed by Na-tripolyphosphate. It is interesting to note from Fig. 2b that at low adsorption levels, there is virtually no desorption by either reagents. Also, the adsorption level at which desorption begins is found to be the highest for the nonionic polymer. When the polymer is adsorbed with a flat configuration or at high energy sites at low levels, phosphate at the

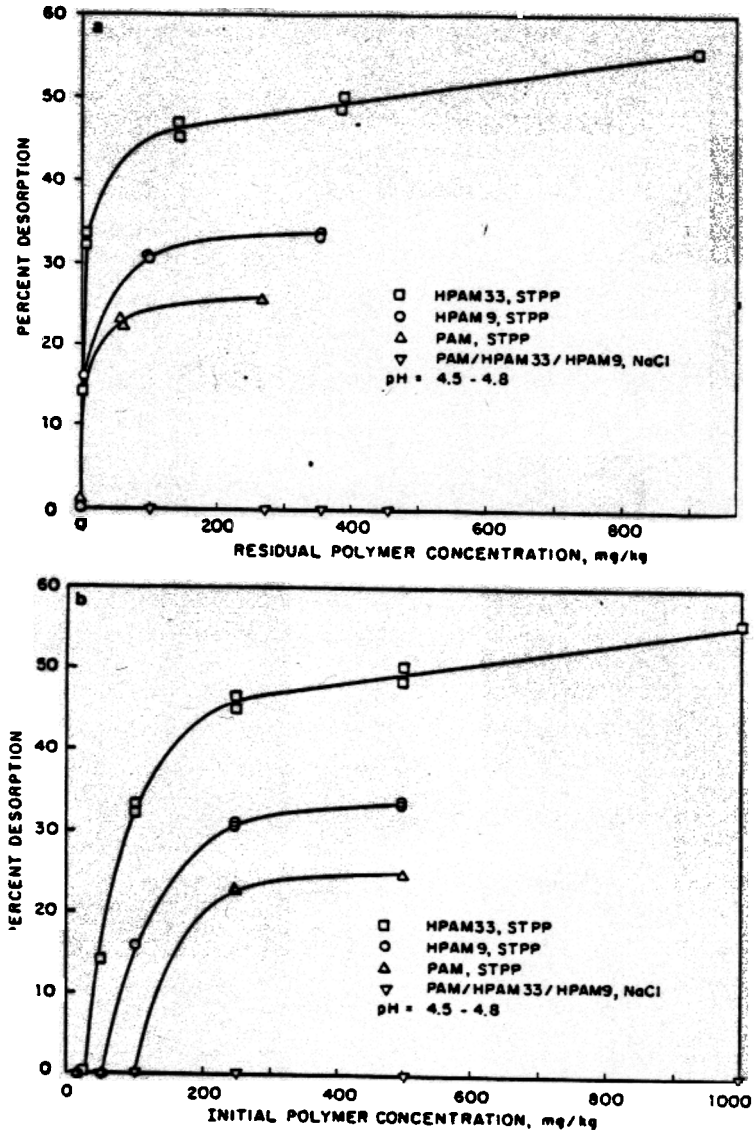

FIG. 2. (a) Percentage desorption of polyacrylamide and hydrolyzed polyacrylamides upon dilution with 5×10^{-2} kmole/m^3 sodium tripolyphosphate (STPP) and 3×10^{-2} kmole/m^3 sodium chloride solutions as a function of residual polymer concentration. (b) Percentage desorption of polyacrylamide and hydrolyzed polyacrylamides upon dilution with 5×10^{-2} kmole/m^3 sodium tripolyphosphate and 3×10^{-2} kmole/m^3 sodium chloride solutions as a function of initial polymer concentration.

present level of addition is unable to compete as effectively with the polymers for adsorption sites. On the other hand, the fact that there is only partial desorption even at the highest polymer level tested suggests that the fraction of the polymers that adsorb on high energy sites might not be amenable to desorption. It is however possible that the concentration of phosphate is not sufficient to cause any further desorption under these conditions. The data

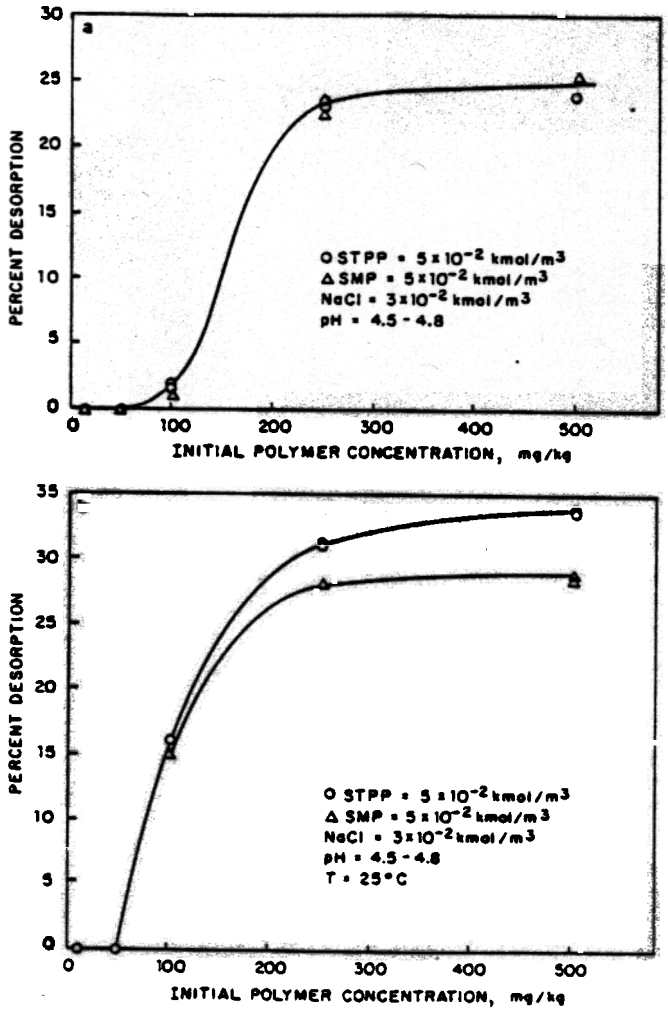

FIG. 3. (a) Percentage desorption of polyacrylamide upon dilution with sodium tripolyphosphate (STPP) and sodium metaphosphate (SMP) as a function of initial polymer concentration. (b) Percentage desorption of 9% hydrolyzed polyacrylamide upon dilution with sodium tripolyphosphate (STPP) and sodium metaphosphate (SMP) as a function of initial polymer concentration.

given in Fig. 2b indicates that, even though the percentage desorption is highest for the 33% hydrolyzed polymer the actual amount in milligrams desorbed is about the same for all the three polymers. The latter can be considered to suggest that the phosphate at 5×10^{-2} kmole/m^3 level is able to displace the polymer from a certain maximum number of sites and in this case, this number is not markedly dependent on the polymer. Furthermore, the data also suggests that the number of contact points per polymer at high polymer levels is about the same in the present system for all polymers. Additional tests at higher levels of phosphate as well as simultaneous measurements of the phosphate uptake by the solid is expected to provide more information on the mechanism of polymer adsorption.

The extent of polymer desorption that can be attained can indeed be expected to depend

upon the type of inorganic competing agent. In this study the desorption capacity of yet another phosphate, sodium metaphosphate, was tested. Whereas sodium metaphosphate was as effective as the tripolyphosphate in desorbing the nonionic polyacrylamide, it desorbed the charged polymer to a lesser extent than the latter (see Figs. 3a and b).

It is seen that the charge of the inorganic additive might be an important factor responsible for determining the extent of desorption of charged polymers. Upon dissolution, sodium tripolyphosphate possesses an average charge of -1.667 per every phosphorous atom in the chain. In comparison, sodium metaphosphate exhibits an average charge of -1.154 per phosphorous atom. The proposed mechanism of adsorption for hydrolyzed polyacrylamide on kaolinite involves hydrogen bonding with electrostatic repulsion superimposed upon it whereas the mechanism of adsorption for nonionic polyacrylamide is primarily due to hydrogen bonding. The phosphate species, which are highly charged in comparison to chloride (NaCl), can contribute toward increased electrostatic repulsion and thus cause desorption of the anionic polymer. Phosphates have been known to specifically adsorb on kaolinite and increase the negative charge characteristics of it. The above considerations are supported by the fact that the metaphosphate, which possesses a lesser charge, produces a lower desorption than the tripolyphosphate.

On the basis of the same reasoning a difference in phosphate charge density should not be expected to have any effect on the desorption of the nonionic PAM, since its adsorption depends only on hydrogen bonding. This is found to be the case as seen in Fig. 3a where the tripolyphosphate and the metaphosphate are compared as competing agents against nonionic PAM.

The competition between adsorbed polymer and bulk polymer for available sites was tested by first adsorbing labeled polyacrylamide from a 100 mg/kg solution and subsequently adding a diluent containing nonradioactive polyacrylamide of the same charge density to obtain an initial concentration of it at 500 mg/kg. Desorption of the ^{14}C-labeled polymer could thus be easily determined. At the 100 mg/kg initial ^{14}C-labeled polymer concentration tested, interestingly, the nonradioactive polyacrylamide (500 mg/kg) caused more desorption than either the tripolyphosphate or metaphosphate. It is to be recalled that NaCl itself produced no detectable desorption of the polyacrylamide (see Table I).

Evidently, under the dynamic equilibrium that prevails in the system when segments of a polymer molecule detach, other polymer molecules can begin to occupy the vacated sites and in some cases cause detachment of the entire molecule that was originally present on the surface.

SUMMARY

Polyacrylamides and hydrolyzed polyacrylamides are desorbed from the surface of kaolinite by tripolyphosphate and metaphosphate while reduction in polymer concentration by dilution alone produced no such desorption. The nonionic polyacrylamide which adsorbed in maximum amounts on kaolinite desorbed least and the 33% anionic polyacrylamide–polyacrylic acid copolymer which adsorbed least had as much as 56% of it desorbed upon diluting a 1000 mg/kg polymer solution with 5×10^{-2} kmole/m^3 sodium tripolyphosphate. The extent of desorption depended strongly on the initial adsorption

TABLE I

Effect of Inorganic Competing Agent on Polymer Desorption

Competing agent	Concentration (kmole/m^3)	Desorption (%)
STPP	5.0×10^{-2}	1.8
SMP	5.0×10^{-2}	2.0
Polyacrylamide[a]	1.5×10^{-4}	5.75
NaCl	1.5×10^{-2}	0
NaCl	5.0×10^{-1}	0

[a] Initial concentration = 100 mg/kg.

level; no desorption could in fact be obtained using phosphates under the test concentration conditions at low surface coverages where the polymer is adsorbed possibly with a flat configuration.

The charge of the inorganic additive is also an important factor in determining the desorption of charged polymers. Sodium metaphosphate was less effective in desorbing the HPAM9 and HPAM33 than the more anionic tripolyphosphate whereas in the case of the nonionic polyacrylamide both performed equally. NaCl on the other hand produced no desorption of the polymers. Adsorption of the phosphates on the kaolinite contributing to an increase in the electrostatic repulsion between the kaolinite and the negatively charged polymer species is considered to be a governing mechanism for the above behavior.

Interestingly, even though dilution itself did not produce any measurable desorption, introduction of additional polymers was found to produce some desorption of the polymer originally adsorbed on the kaolinite. It is concluded that polymer desorption does not normally take place due to the difficulty in achieving detachment of all the adsorbed segments of a polymer molecule simultaneously. However, if the vacated sites can be blocked by other agents then desorption can indeed occur.

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