Effects of Inorganic and Organic Additives on the Adsorption of Nonionic Polyacrylamide on Hematite

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The effects of inorganic anions such as chloride, sulfate, and phosphate on the adsorption of nonionic polyacrylamide on hematite are studied. Adsorption of the polymer is reduced in all cases, with complete depression by phosphate. The relative effectiveness of these anions in reducing polymer adsorption increases in the order chloride < sulfate < phosphate, a trend which corresponds to the relative stabilities of the anion–Fe^{3+} complex formation. The effectiveness of sulfate and phosphate in competing with the polymer for surface sites is explained in terms of the strong interaction of these anions with $FeOH_2^+$ and FeOH by ligand exchange, replacing the surface hydroxyl groups. Since at lower pH there is higher interaction of these anions with the surface, the effect of pH on polymer adsorption is reversed. Urea is also found to decrease polymer adsorption. In this case, the phenomenon is due to H-bonding of the urea with the surface hydroxyls, depleting adsorption sites for the polymer.

INTRODUCTION

The adsorption of water-soluble polymers on hydrophilic solid surfaces is predominantly governed by electrostatic interactions, H-bonding, and solvation forces. For charged polymers, electrostatic interaction is significant and parameters like pH and ionic strength of the solution become determining factors of adsorption. If the surface and the polymer carry opposite charges, both electrostatic and H-bonding forces favor the adsorption process. If, however, they carry similar charges, then adsorption is determined by a competition of attractive H-bonding force and repulsive electrostatic interaction. For uncharged polymers, only H-bonding (1–8) and solvation forces, the latter of which always act against adsorption, are considered to be important. In spite of that, adsorption of nonionic polymers on oxide minerals has been found to be pH dependent (5, 8). This has been studied systematically for adsorption of polyacrylamide on different oxides and the pH dependence observed has been attributed to the site dependence of H-bonding (8). Although H-bonding is not considered to be an electrostatic type interaction, the functional group of the polymer (C=O) which is engaged in the bonding mechanism does carry a net electronegativity, and interaction of it with surface sites would depend on the relative electropositivity of the latter, which have been proposed to be the MOH_2^+ and MOH groups. Such a dependence then manifests itself in pH dependence of H-bonding.

In this study, the effects of additives which can adsorb onto and compete with the polymer for these adsorption sites are investigated. The competing agents chosen for this purpose are negative inorganic anions varying in charges and affinities for the oxide surface such as chloride, sulfate, and phosphate. The influence of pH on polymer adsorption in the presence of these anions is also studied. The effect of an organic compound, urea, is also investigated in view of its proposed character as a H-bond breaker.

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EXPERIMENTAL

The hematite used is a synthetic oxide from Alfa Chemicals. It is in powder form with a specific surface area of 8.4 m^2/g as measured by BET technique using N_2 as adsorbate. The point of zero charge is measured to be 7.5 using the zeta-meter.

The nonionic polyacrylamide is synthesized using radiation induced precipitation method with a ^{60}Co source. It is labeled with ^{14}C as radio-tracer. From viscometry, the average molecular weight is determined to be 0.7 million Da. By adsorbing the polymer onto a mineral support and measuring the zeta potential of the polymer covered mineral, it is verified that the polymer is nonionic in nature (8).

The experimental procedure consists of a preconditioning step and the conditioning of the mineral with polymer. In preconditioning, the mineral is added to the solvent containing the necessary salts and adjusted to the required pH. This is a wetting stage to ensure complete dispersion of the fine mineral particles. Polymer solution adjusted to the same final conditions of the solvent is then added. The preconditioning time, determined from the final constant pH value, and the polymer adsorption time, determined from kinetic studies, are 3 and 4 h, respectively. Mixing in both cases is facilitated by a mechanical wrist-action shaker. In all cases, the final solid/liquid weight ratio of the suspension is 0.03. The amount of polymer adsorbed is determined by the depletion method. The polymer concentrations before and after adsorption are determined from the radiations of the ^{14}C labeled polymer samples using a scintillation counter.

RESULTS AND DISCUSSIONS

Effect of Anions

The effects of chloride, sulfate, and phosphate on polyacrylamide adsorption on Fe_2O_3

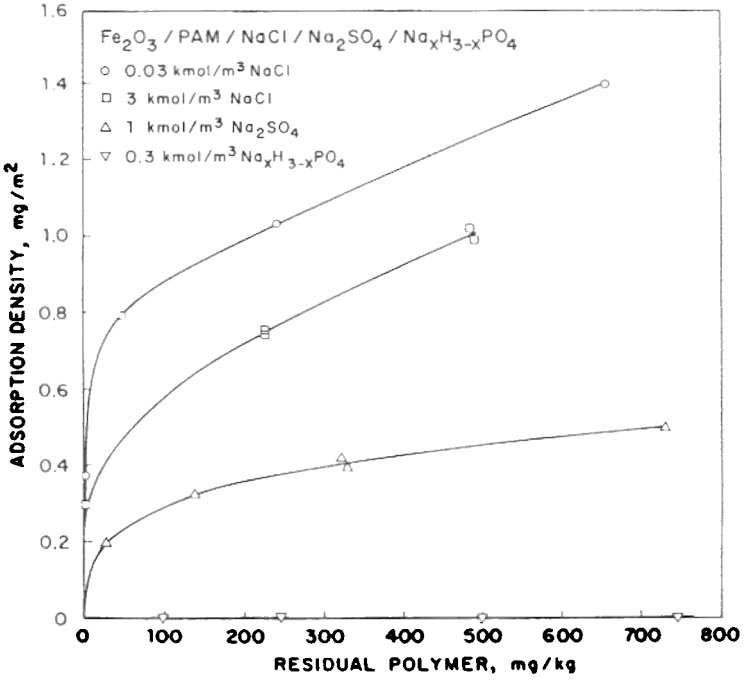

FIG. 1. Effects of chloride, sulfate, and phosphate on PAM adsorption on Fe_2O_3 at pH 6.6.

at pH 6.6 are shown in Fig. 1. The concentrations of these anions, with sodium as the counterion, are 3 kmol/m^3, 1 kmol/m^3, and 0.3 kmol/m^3 so that comparison of these ions is made at a constant ionic strength. At pH 6.6 where the Fe_2O_3 has a net positive charge, the presence of anions reduces polymer adsorption significantly in the order chloride < sulfate < phosphate, with complete depression of the PAM adsorption by phosphate. This is due to interactions of the anions with adsorption sites on the Fe_2O_3 thus reducing the number of adsorption sites available for the polymer.

The order by which the anions depress adsorption of PAM on Fe_2O_3 follows the sequence of affinities of the anions for Fe_2O_3, namely, chloride < sulfate < phosphate. As expected, chloride, being monovalent, has a lower affinity for Fe_2O_3 than its higher valence counterparts, sulfate and phosphate. However, it should be noted that even though electrostatic interaction contributes to the anion adsorption on Fe_2O_3, it is not the sole factor. Phosphoric acid has three dissociation constants and at pH 6.6, even though 80% of the total phosphate is in monovalent form $H_2PO_4^-$, and 20% is in the bivalent form HPO_4^{2-}, phosphate interacts more strongly with Fe_2O_3 than sulfate, 100% of which is in the bivalent form SO_4^{2-}. Even though the adsorption of both sulfate and phosphate has been shown to be of "high affinity" type (9, 10), the higher (9) and stronger (11) adsorption of phosphate over sulfate has in fact been shown elsewhere. In addition, it has also been shown that phosphate can be used as an agent to displace adsorbed sulfate from soils (12). The unusually high affinity of phosphate for oxide minerals and clays is thought to be due to the geometric compatibility between the phosphate ions and the oxide surface structure (13), and the effective role of phosphate in desorbing polymers from clays has also been studied (14). It has been proposed also that not only does phosphate adsorb on the positive and neutral sites but also on the negative sites as described by the equilibria (15)

$$FeOH_2^+ + H_2PO_4^- \leftrightarrow FeH_2PO_4 + H_2O$$

$$FeOH_2^+ + HPO_4^{2-} \leftrightarrow FeHPO_4^- + H_2O$$

$$FeOH + H_2PO_4^- \leftrightarrow FeH_2PO_4 + OH^-$$

$$FeOH + HPO_4^{2-} \leftrightarrow FeHPO_4^- + OH^-$$

$$FeO^- + H_2PO_4^- \leftrightarrow FeHPO_4^- + OH^-$$

$$FeO^- + HPO_4^{2-} \leftrightarrow FePO_4^{2-} + OH^-$$

Similarly, for sulfate adsorption, we propose

$$FeOH_2^+ + SO_4^{2-} \leftrightarrow FeSO_4^- + H_2O$$

$$FeOH + SO_4^{2-} \leftrightarrow FeSO_4^- + OH^-$$

The effectiveness by which sulfate and phosphate ions compete with polyacrylamide for adsorption sites on Fe_2O_3 merits further discussion, in particular, that which concerns their mechanisms of adsorption. In contrast to the nonspecific type of adsorption by monovalent ions such as Cl^- and NO_3^-, sulfate and phosphate bond to the Fe_2O_3 surface by specific adsorption, and when present in excess cause charge reversal of the mineral. In fact, under certain conditions, phosphate can be considered to be a potential determining ion for hematite and other oxides (10). It has been proposed, from infrared spectroscopic studies, that both sulfate and phosphate ions adsorb by ligand exchange with exposed surface FeOH and $FeOH_2^+$ groups to form binuclear complexes (9, 16). Thus, formation of these complexes involves the exchange or displacement of two adjacent surface hydroxyls or water from the Fe^{3+} coordination. This model strongly supports the proposed hypothesis that, for an oxide mineral, the MeOH and $MeOH_2^+$ surface groups are the adsorption sites for polyacrylamide, and that polymer adsorption takes place through H-bonding with these surface hydroxyls (8).

Effect of pH

Interactions of the above anions with Fe_2O_3 are stronger at lower pH where the charge difference between the anion and the Fe_2O_3 is higher. Consequently, depression of polymer

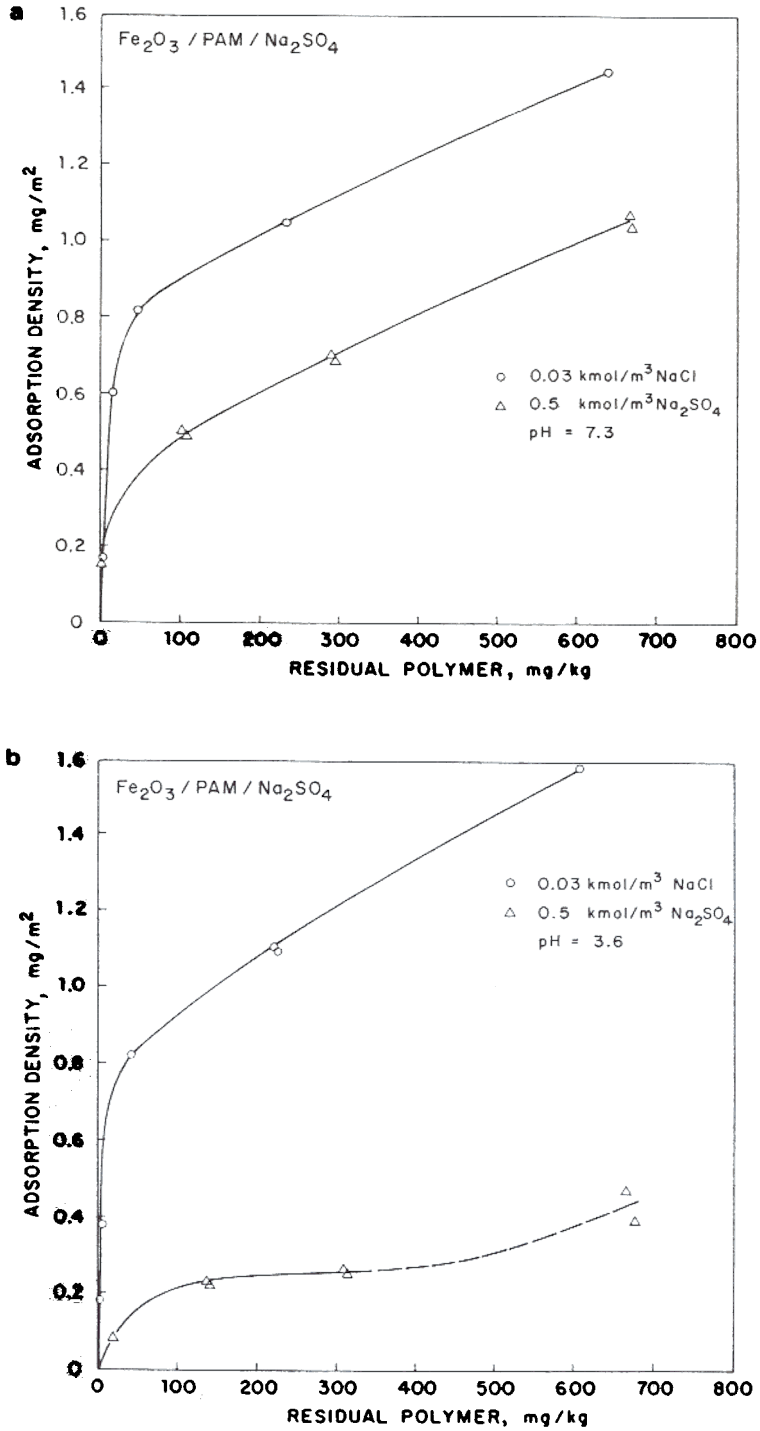

FIG. 2. (a) Effect of 0.5 kmol/m³ Na_2SO_4 on PAM adsorption on Fe_2O_3 at pH 7.3. (b) Effect of 0.5 kmol/m³ Na_2SO_4 on PAM adsorption on Fe_2O_3 at pH 3.6. (c) Effect of pH on PAM adsorption in 1 kmol/m³ Na_2SO_4.

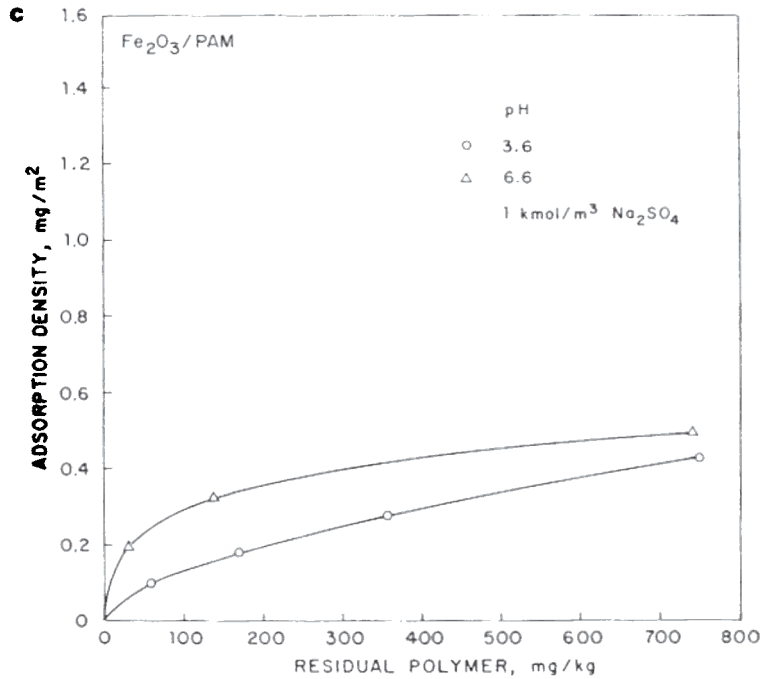

FIG. 2—*Continued*

adsorption due to competition from these anions is expected to be more significant at lower pH. This is indeed observed upon comparison of results obtained when 0.5 kmol/m^3 sulfate is added at pH 7.3 and pH 3.6 (Fig. 2a and 2b, respectively): the percent reduction in polymer adsorption at pH 3.6 exceeds that at pH 7.3 by the higher interaction of sulfate with the oxide surface at lower pH. In this case, not only is adsorption of the anion weaker at neutral pH but the higher proportion of neutral sites also serves to limit the amount of polymer adsorption that is reduced. However, interaction of sulfate with neutral sites is enhanced at higher sulfate concentration (1.0 kmol/m^3), decreasing significantly polymer adsorption even around neutral pH (Fig. 2c). One can infer that the addition of phosphate at low pH will also result in complete depression of PAM adsorption since adsorption of phosphate increases with decrease in pH (10). The adsorption densities of sulfate and phosphate on Fe_2O_3 at pH 3.5 have in fact been measured to be 85 and 170 μmol/g, respectively (9).

The pH dependence of anion–Fe_2O_3 interaction and the resultant depression of polymer adsorption thus inverts the trend by which polymer adsorption changes with pH. In the presence of nonspecifically adsorbing anions like chloride, the original trend (PAM adsorption increases with decrease in pH (8)) is maintained, as can be seen from Figs. 3a and 3b.

The preferential adsorption of PAM on positive and neutral sites does not imply that polymer cannot adsorb on the negative sites since, under basic conditions where the surface is negatively charged, adsorption can still take place. H-bonding in this case is probably between the weakly acidic NH_2 group on the polymer and the basic MO^- on the oxide. Adsorption is thus lower due to the weaker H-bond and to electrostatic repulsion between the negatively charged surface and the polymer if the latter had undergone some hydrolysis under basic conditions. Under low adsorption conditions at pH 12, addition of 0.5 kmol/m^3 sulfate does not reduce polymer adsorption

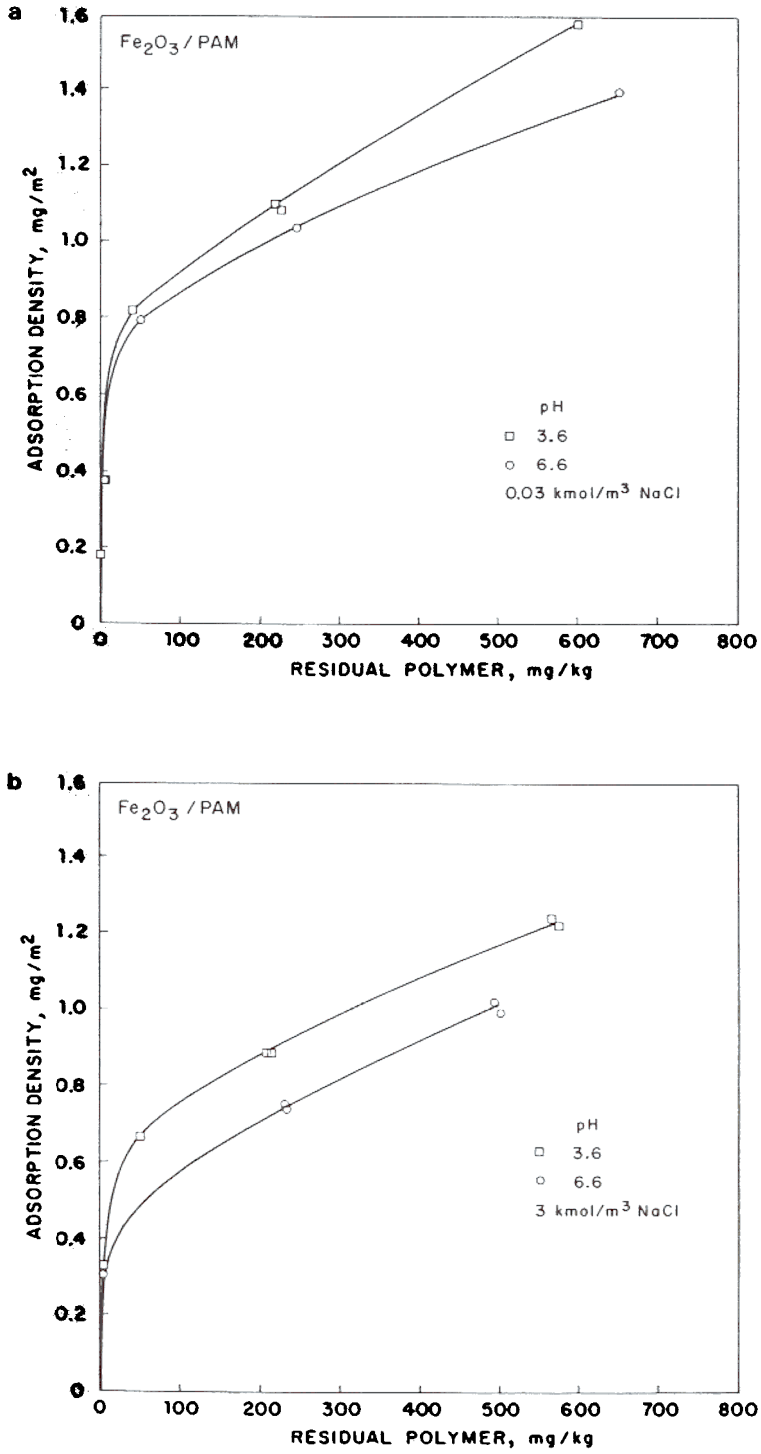

FIG. 3. (a) Effect of pH on PAM adsorption in 0.03 kmol/m³ NaCl. (b) Effect of pH on PAM adsorption in 3 kmol/m³ NaCl.

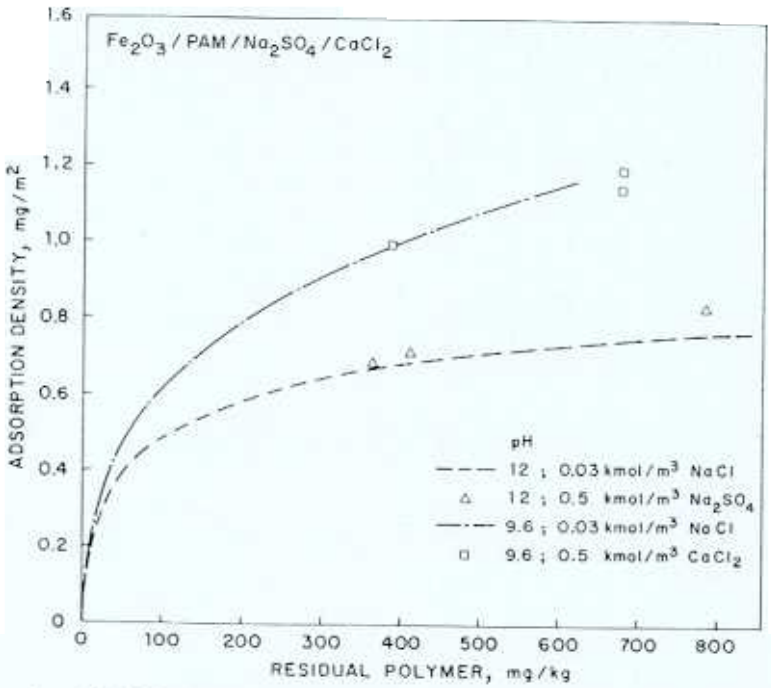

FIG. 4. Adsorption of PAM in the presence of Na_2SO_4 (0.5 kmol/m³; pH 12) and $CaCl_2$ (0.5 kmol/m³ pH 9.6).

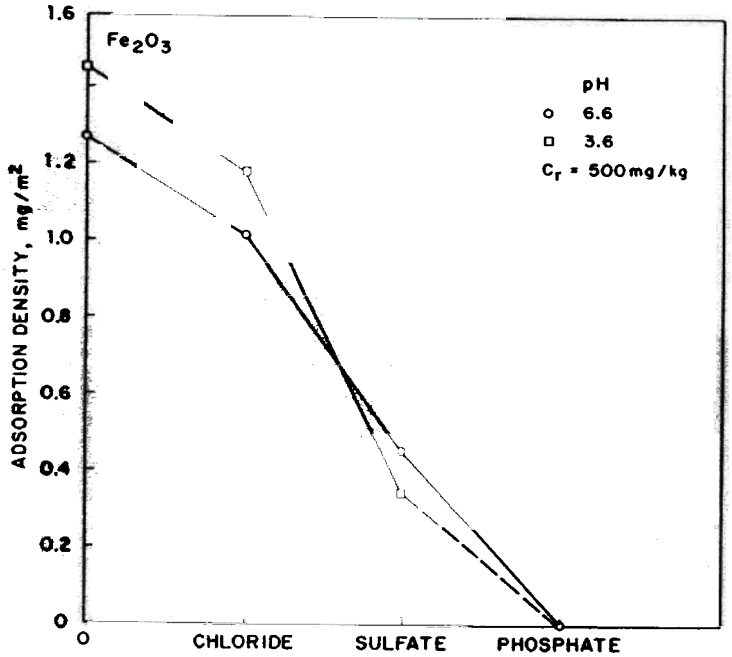

FIG. 5. Summary of effects of chloride, sulfate, and phosphate on PAM adsorption on Fe_2O_3 at pH 3.6 and 6.6.

since the sulfate does not adsorb on the negatively charged surface (Fig. 4). On the contrary, a slight increase in adsorption of the polymer is observed. This may be due to "salting-out" effect of the polymer by the sulfate which is observed when polymer–surface interaction is weak. At a lower but still basic pH (9.6) where there are still some neutral sites on the oxide surface, addition of 0.5 kmol/m^3 $CaCl_2$ does not alter the adsorption level of the polymer even though the calcium ions do adsorb on the negative sites. This suggests that polymer adsorption in this case is still taking place preferentially on the neutral sites. It is not totally ruled out, however, that the cations can replace some polymers from the surface but that this effect is undetected and/or is counter-balanced by salting-out effect of the polymer by the cation. Interestingly, an enhancement in polymer adsorption by cation activation is not observed.

From the above results, it is evident that complexing agents such as sulfate and phosphate compete very successfully with polymer for adsorption sites on the Fe_2O_3 and dramatically reduce the level of polymer adsorbed. A summary of results is given in Table I and graphically represented in Fig. 5.

The addition of anions may cause complexation between the anions and the dissolved species from the oxide. Calculations of such complexation for the species Fe^{3+} and these anions in the bulk solution using equilibrium constants from Sillen and Martell (17) show that formation of these complexes is insignificantly small due to the low solubility of the oxide. These calculations also show that the relative stabilities of the Fe^{3+}–phosphate, Fe^{3+}–sulfate, and Fe^{3+}–chloride complexes decrease in the order by which the corresponding anions reduce polymer adsorption on Fe_2O_3. If the stabilities of these complexes are maintained at the interface, then the relative effectiveness by which the anions depress polymer adsorption is comprehensible.

TABLE I

Summary of Effects of Chloride, Sulfate, and Phosphate on Polyacrylamide Adsorption on Fe_2O_3 (Residual Concentration = 500 mg/kg)

	Percent reduction in polymer adsorbed	
Anions	pH 3.6	pH 6.6
1.0 kmol/m^3 chloride	—	6.3
3.0 kmol/m^3 chloride	19.3	19.7
0.5 kmol/m^3 sulfate	77.9	32.3
1.0 kmol/m^3 sulfate	76.6	64.6
0.3 kmol/m^3 phosphate	—	100

Effect of Urea

It has been shown above that competing agents which adsorb specifically on the mineral surface and thus deplete adsorption sites are highly effective in depressing polymer adsorption. Another way to reduce the level of polymer adsorbed is by the use of molecules which can affect the bonding mechanism, namely H-bonding between the polymer and the surface hydroxyls. For this purpose, urea is chosen since it is believed to be a H-bond breaker by virtue of its own tendency to form H-bond. The effect of urea on H-bonding in other systems have been studied elsewhere (18, 19).

In solution, urea acts as a "structure-maker" (20) which implies that it can salt-out polymer, a phenomenon which generally leads to increase in polymer at the interface. But the results in Fig. 6 show that the polymer adsorption is decreased in the presence of urea. This is attributed to the overriding effect of urea at the interface. Since urea is also an amide (carbamide), adsorption of it on the oxide surface is not surprising. In fact, it is believed that urea is a stronger H-bonding base than other amides due to resonance stabilization (21), therefore interaction of it with oxide surface hydroxyls can be expected to be stronger than that of polyacrylamide.

An important point worth noting here is the mechanism by which polymer adsorption is reduced by the various competing agents. While sulfate and phosphate deplete adsorption sites by ligand exchange with $FeOH_2^+$ and

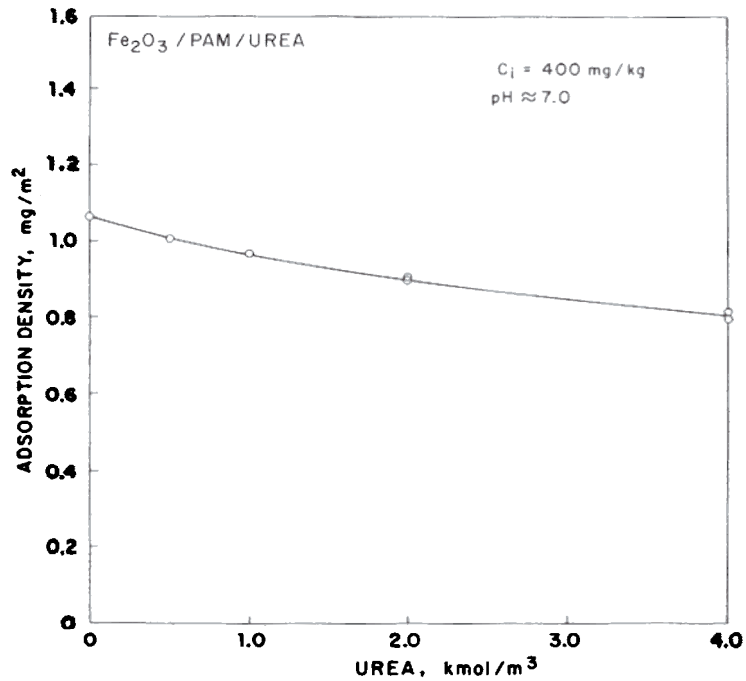

FIG. 6. Adsorption of PAM on Fe_2O_3 in the presence of urea at pH 7.

FeOH replacing the surface hydroxyls, urea binds with the surface hydroxyls by H-bonding at the expense of polyacrylamide. In this case, the level by which polymer adsorption is reduced is found to be independent of the mode of addition of urea; irrespective of whether urea is added before, together with, or after the polymer, the reduction in polymer adsorbed is the same. This is a consequence of the reversibility polymer in adsorption.

CONCLUSIONS

Polyacrylamide adsorption on Fe_2O_3 is decreased in the presence of competing anions such as chloride, sulfate, and phosphate. While the effect of chloride is less marked, significant reduction by sulfate and complete depression by phosphate are obtained. This can be explained by taking into consideration the specific interactions of sulfate and phosphate with Fe_2O_3 by ligand exchange, replacing surface hydroxyls which are adsorption sites for the polymer. These effects are more significant at lower pH due to higher interaction of anions with the more positively charged surface. Thus, the effectiveness by which these anions reduce polymer adsorption follows, in increasing order, chloride < sulfate < phosphate. This is also the order of relative stability of the anion complexation with Fe^{3+}.

Urea is also found to reduce polyacrylamide adsorption on Fe_2O_3. Contrary to the case of sulfate and phosphate where surface hydroxyls are replaced, this is attributed to H-bonding of urea itself with the surface hydroxyls thus depleting adsorption sites for the polymer.

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