

Adsorption of Polyacrylamide on Oxide Minerals

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The adsorption of nonionic polyacrylamide on a series of oxide minerals is studied. The results show that adsorption of the polymer increases with increase in the point of zero charge of the oxide. A strong pH dependence of the adsorption density is observed for all oxides, which is further correlated with the distribution of the positive and neutral sites on the surface. This is attributed to the favorable H bonding between the electronegative C=O group of the polymer and the proton-donating groups on the oxide surface that are constituted by these sites. The solvation of oxide cations is also found to influence polymer adsorption. As the energy of the oxide cation solvation increases, adsorption of the polymer on the corresponding oxide decreases. Such an inverse relationship is due to competition between oxide-solvent and oxide-polymer interactions.

Introduction

Polymer adsorption is encountered in numerous industrial applications, where a good knowledge of the adsorption mechanism is important for the economic and technical success of the process. In mineral beneficiation, for example, polymers are added for depression, flocculation, or dispersion of the minerals. In this case, the polymer encounters minerals with different surface properties, and the key to successful beneficiation lies in the selectivity of the polymer adsorption. An application of such selectivity is seen in the case of iron ore processing at the Tilden Mines, where starch is added to flocculate selectively the iron oxide from silica in the desliming stage prior to flotation.¹ Another example is the microflotation of a mixture of hematite and quartz using dodecylamine where polyacrylamide is used to depress hematite selectively while quartz is completely floated.² The reason for the selectivity of the affinity of polymer for one oxide over another is not completely understood due to a limited knowledge of the adsorption mechanism. The adsorption of polymers can also lead to detrimental effects as in the case of enhanced oil recovery, where polymer is used as a mobility control agent; in this case, the adsorption of polymer onto mineral surfaces leads to a loss in viscosity of the polymer slug resulting in delayed oil recovery. Other industrial processes involving polymers include detergency, food processing, and biotechnology.

In view of the importance of polymer adsorption and its applications, the present work entails a study of adsorption of a nonionic polymer, polyacrylamide, on a series of well-characterized oxides to determine the role of surface properties in relation to the nature of polymer-surface interaction.

Polymer Adsorption

Progress made in the past 30 years on polymer adsorption has encompassed both experimental and theoretical aspects. Experimentally, the emphasis has been on the development of optical and spectroscopic techniques to study the adsorbed layer. Theoretically, adsorption models have evolved from simple gas adsorption models³ to the random walk approach^{4,5} to statistical mechanical treatment.⁶⁻⁹ The last method has been under extensive development over the past 2 decades and seems to be a reasonable approach to treat polymer adsorption since it emphasizes the configurational entropy and energy. In spite of these developments, theoretical treatment and

experimentation in polymer adsorption have not fully concurred due to the theoretical requirement of a high degree of ideality in model systems and of the numerous parameters, which are not readily available. Nevertheless, theoretical predictions have provided a useful guide in the study of polymer adsorption behavior. However, the basic information which reflects the mechanism of the process (such as the type of bonding between the polymer, solvent, and surface, the role of surface properties adsorption sites, and the energy and driving force involved in the process) is still to be obtained experimentally.

Factors Governing Adsorption. The system variables that affect polymer adsorption are similar to those that govern any adsorption process from solution. These factors include the physical and chemical nature of the adsorbent and adsorbate, solvent power, and temperature.

1. Nature of the Adsorbent. The type of surface site is as important as the functional group of the polymer in adsorption. The characteristics of the solid surface, like surface charge, potential, and the degree of solvation, are all dependent on the solvent properties and temperature of the system. In the case of oxides, for example, these properties depend on the pH of the solution since H⁺ and OH⁻ are the potential-determining ions.

The solubility behavior of the adsorbent is not to be neglected. For a solid which undergoes significant dissolution, the kinetics of dissolution and polymer adsorption have to be carefully considered, particularly if the adsorbed polymer can be detached upon dissolution of the adsorbent and the ion-polymer complex does not re-adsorb. Apart from the chemical nature of the adsorbent, the physical properties such as porosity and particle size are also important.

2. Chemical Nature of Polymer. The type of interaction between the polymer and the solid surface is determined by the chemical structure of the polymer relative to that of the surface. For example, a nonpolar functional group will react favorably with a hydrophobic site on a surface, and a polar group will show affinity for a hydrophilic site. If the polymer is charged, electrostatic interaction plays a major role in adsorption, and the ionic strength and pH of the solution become important parameters. For uncharged polymers, electrostatic forces

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become unimportant, and H bonding and solvation become predominant.

3. Molecular Weight. In general, for nonporous adsorbents, polymer adsorption increases with molecular weight, although the degree of dependence is markedly influenced by the solvent power. For a good solvent, all the statistical theories predict a weak dependence of adsorption on molecular weight.⁹⁻¹⁴ For a poor solvent,¹⁰⁻¹⁴ however, the theories of Frisch, Simha, and Eirich^{4,5} and of Hoeve¹²⁻¹⁴ predict a square root dependence. Silberberg's theory¹¹ also predicts a square root dependence for low molecular weight polymers, but for high molecular weight polymers, a limiting value is predicted. A linear function is predicted for low molecular weight from the models of Roe¹⁰ and of Scheutjens and Fleer,^{8,9} with leveling off at high molecular weight for Roe's theory.

Experimentally, however, molecular weight dependence of adsorption can usually be described qualitatively only due to the polydispersity of the polymers.

4. Solvent Power. The conformation of a polymer in bulk or at the interface is dependent on the polymer-solvent interaction defined by the Flory-Huggins parameter which in turn is governed by the solvent power. In general, the experimentally observed trend is a decrease in adsorption with an increase in solvent power. However, it is possible that a reverse trend can occur if, for example, a poor solvent interacts significantly with the adsorbent surface. The resultant competition between solvent and polymer molecules for surface sites can result in a decreased or even negative adsorption.

5. Temperature. The dependence of polymer adsorption on temperature varies with the system studied. For example, the adsorption of polyisobutene from benzene onto carbon black has been reported to decrease with temperature,¹⁵ while an increase has been found for the system poly(vinyl acetate)/metal powders.¹⁶ The overall response of adsorption depends on the individual effects of temperature on (i) solubility of the polymer, which is characterized by the polymer-solvent interaction and the free energy of mixing, and (ii) the state of solvation of the surface and the polymer.

From the temperature dependence, thermodynamic properties of adsorption can be evaluated. The heat of adsorption has been calculated this way by using the Clausius-Clapeyron equation,¹⁶ which under isosteric conditions is given by

$$\frac{\Delta H}{R} = \frac{d(\ln C)}{d(1/T)} \quad (1)$$

However, this method of enthalpy calculation assumes that (i) the adsorption process is reversible and (ii) the enthalpy is constant over the temperature range studied. Neither of these assumptions is unambiguously valid. In fact, a contradiction has been found for the system poly(ethylene glycol)/silica,¹⁷ where the enthalpy evaluated by the Clausius-Clapeyron equation is positive while that obtained calorimetrically is negative. The results obtained from calorimetry should be more reliable since this technique is direct and does not involve any assumptions such as those inherent in model equations. Using calorimetry, the enthalpy change can also be measured as a function

Table I. Properties of Oxides

oxide	surface area, m ² /g	pzc
		8.4
		2.1
		5.5
		7.8
		6.1
		0.7

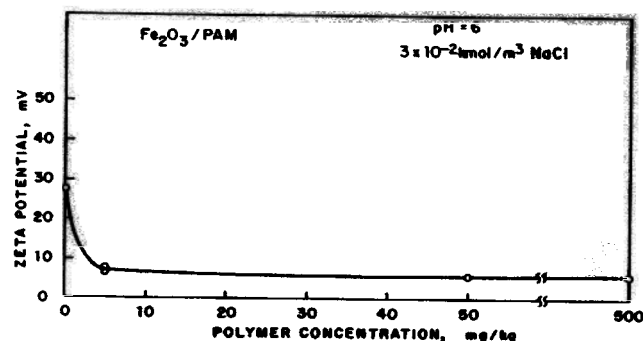


Figure 1. ζ potential of Fe_2O_3 as a function of PAM concentration.

of temperature. Note that if polymer adsorption is endothermic, the process is entropically driven. According to Gibb's equation

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

If ΔH is positive, then ΔS also must be positive, and the absolute magnitude of $T\Delta S$ must be greater than the absolute magnitude of ΔH . Since the polymer loses translational freedom upon adsorption and thereby decreases the entropy, a positive ΔS implies that this decrease is exceeded by the increase in entropy gain from the release of bound hydration water around the polymer and/or at the solid surface.

The present study deals with the nature of the adsorbent surface and its effects on polymer adsorption. This is carried out by using different substrates, namely, oxides, and varying their surface properties by changing the solution pH.

Materials and Methods

Minerals. The oxide minerals used are Fe_2O_3 , Cr_2O_3 , Al_2O_3 , TiO_2 (anatase), SnO_2 , and SiO_2 . All the samples are synthetic oxides acquired commercially from Alfa Chemicals and used as received except for SiO_2 , which is natural Brazilian quartz prepared by wet grinding and leaching. The surface areas of the powdered samples are determined by N_2 adsorption using the BET technique, and the electrokinetic properties measured by using the Zeta Meter are given in Table I.

Polymer. The polymer is a ¹⁴C-labeled nonionic polyacrylamide (PAM) synthesized by using the radiation-induced precipitation method with a ⁶⁰Co source.¹⁸ The average molecular weight determined by viscometry is approximately 0.7 million daltons.¹⁹ The nonionic nature of the polymer has been verified by adsorbing the polymer onto Fe_2O_3 particles and then measuring the electrokinetic properties of the particles. Figure 1 shows the ζ potential results of Fe_2O_3 at pH 6 as a function of polymer concentration. In the absence of polymer, the ζ potential is about +28mV. When the polymer is added up to 500/mg kg, the ζ potential decreases and reaches a constant value of +6mV. This suggests that the Fe_2O_3 particles are coated with the polymer, and the potential measured is that of the partially polymer-coated surface. It is deduced that the polymer has not undergone hydrolysis because if it were hydrolyzed, the negative charge of the

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Table II. ζ Potential of Fe_2O_3 in the Presence of PAM

pH	ζ potential	
	no PAM	500 mg/kg of PAM
		+8
		+7
		+5
		0
		-9

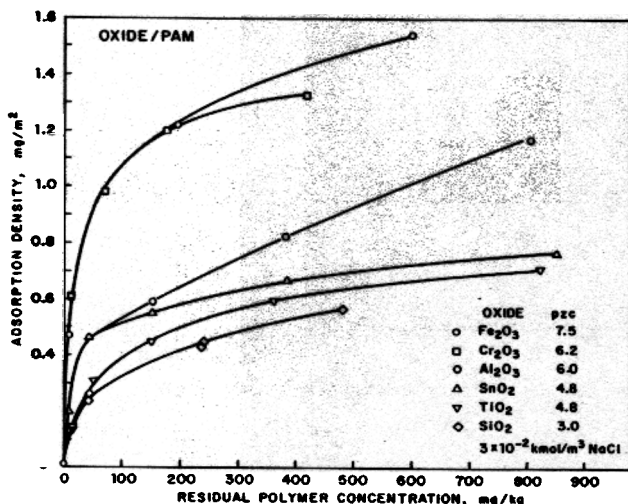


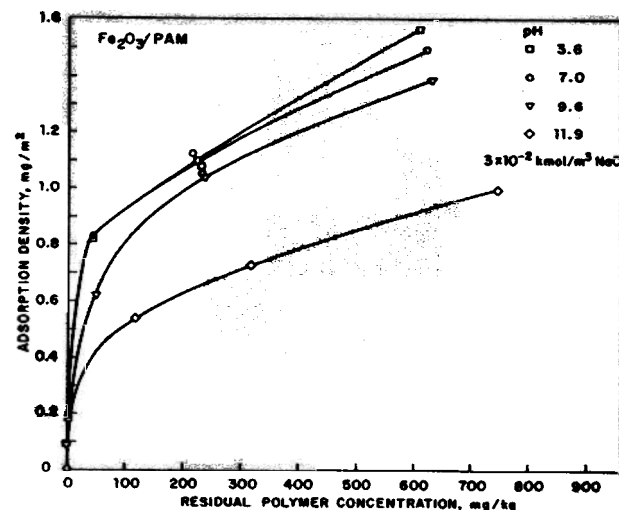
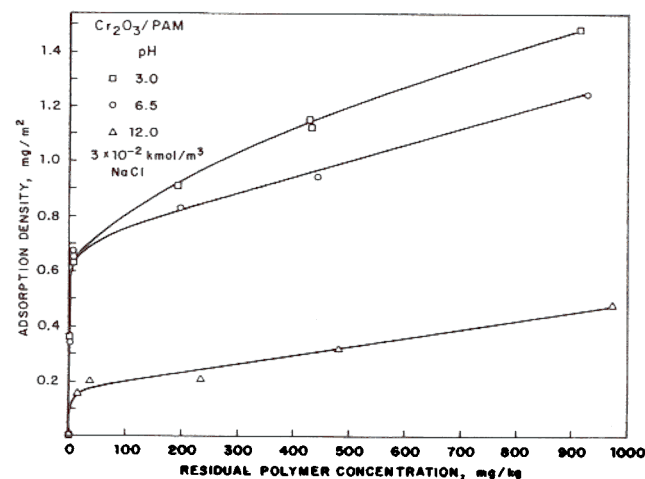
Figure 2. Adsorption isotherms of PAM on oxides.

polymer adsorbed on the Fe_2O_3 would normally be expected to cause a charge reversal and result in a final negative ζ potential.²⁰ Similar measurements made at other pH values are given in Table II. It can be seen from the above table that at all pH values, the presence of adsorbed polymer reduces the magnitude of the ζ potential. The nonionicity of the polymer is most evident at pH 7.5 (pzc), where there is no net charge on the Fe_2O_3 surface and where the adsorbed polymer does not induce any charge either.

Experimental Procedure. The depletion method is used to determine the amount of polymer adsorbed. The mineral is prewetted with the solvent before the addition of polymer. The preconditioning (wetting) time is determined by introducing the mineral into the solvent and measuring the pH change of the suspension with time. A constant bulk pH is taken to be an indication that equilibrium is attained. The polymer solution is then added and the suspension conditioned further at a final solid/liquid = 0.03. The polymer adsorption time is determined from kinetic studies, and adsorption is considered to be complete when the adsorption density remains constant with time. Both prewetting and polymer conditioning of the suspension are accomplished by a wrist-action shaker. For all the studies, the preconditioning and polymer conditioning times are determined, and the appropriate times chosen are 3 and 4 h, respectively. Longer polymer conditioning times are not used, so that any possible degradation of polymer during mixing can be minimized. In tests where the pH is controlled, the equilibrium pH of the suspension after the preconditioning step is noted, and the polymer solution is preadjusted to the corresponding pH before adding to the suspension. In all cases, the ionic strength is maintained at 3×10^{-2} kmol/m³ NaCl, and the temperature ranges from 24 to 26 °C.

Results and Discussion

Adsorption Isotherms. The adsorption densities of the nonionic polyacrylamide on six different oxides at natural pH (from 6 to 8) are plotted in Figure 2 as a function of residual polymer concentration. All the isotherms show a steep rise in the low-concentration region

Figure 3. Effect of pH on PAM adsorption on Fe_2O_3 .Figure 4. Effect of pH on PAM adsorption on Cr_2O_3 .

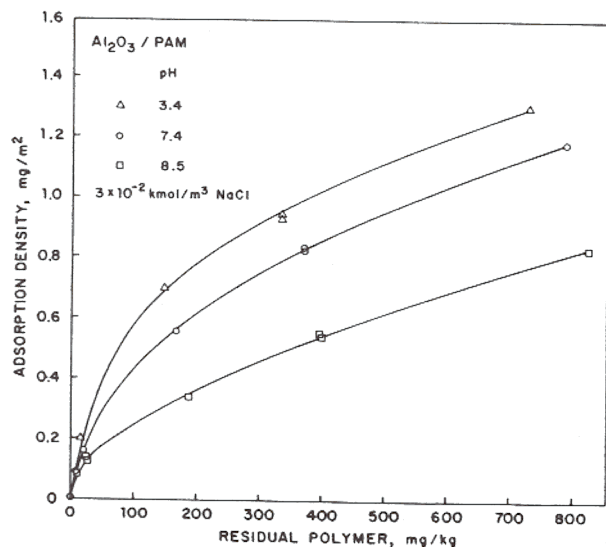
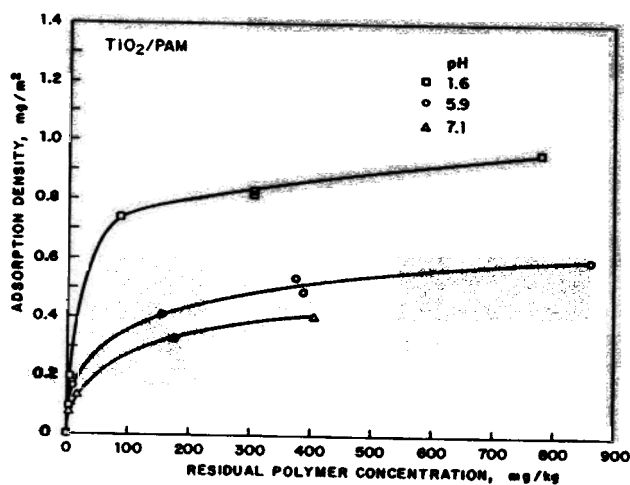
followed gradually by a shallower rise with increase in concentration. This is a high affinity type adsorption isotherm characteristic of polymer adsorption. The different adsorption capacities of the various oxides for the polyacrylamide are evident from these isotherms. The points of zero charge (pzc) of the oxides measured by using electrophoresis are also given in the same figure. A comparison of the values of pzc with the adsorption densities shows that as pzc increases, adsorption of the polymer on the oxide increases. This correlation is interesting because the pH - pzc is a measure of the surface charge of an oxide, and these results show that, in spite of the nonionic nature of the polymer, the surface charge nevertheless plays a role in the adsorption process.

pH Effects. A more detailed investigation of the surface charge effects is carried out by studying adsorption as a function of pH since the H^+ and OH^- are the potential-determining ions for oxides. Figures 3-6 show the results of adsorption densities for Fe_2O_3 , Cr_2O_3 , Al_2O_3 , and TiO_2 at different pH values. In all cases, adsorption decreases with an increase in pH, indicating that adsorption decreases as the surface charge of the oxide increases. This observation, which has also been reported by others,^{21,22} is unexpected at first sight since the polymer, being es-

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 Figure 5. Effect of pH on PAM adsorption on Al_2O_3 .

 Figure 6. Effect of pH on PAM adsorption on TiO_2 .

sentially nonionic, is considered to adsorb by H bonding, and electrostatic interaction should not be significant. At high pH however, the polymer can undergo hydrolysis, and electrostatic repulsion between the hydrolyzed polymer and the negative surface charge reduces adsorption. However, it has been found that polyacrylamide hydrolyzes around pH 10 (ref 18), and the above pH effects cannot be totally attributed to such repulsions because in the case of TiO_2 (Figure 6) all the pH values studied are below the polymer hydrolysis pH.

In considering H bonding between the polyacrylamide and the adsorbent, an examination of the chemical structure of the polymer and the oxide surface species shows that the most probable situation is where the electronegative $\text{C}=\text{O}$ function of the amide acts as a H-bonding base and the oxide surface hydroxyls as H-bonding acid. In this case, not only the neutral undissociated MOH group but also the positive MOH_2^+ group can act as proton donors (Figure 7a). Note that although H bonding is not considered as an electrostatic interaction, the fact that it is a bond between an electronegative and an electropositive group could render it charge dependent. Therefore, the positive MOH_2^+ group should be at least as favorable or even more favorable than the neutral MOH to form an H bond with the $\text{C}=\text{O}$. From Figure 7, it can be seen that the positive and the neutral sites, acting as H-bonding acids, are more favorable for H bonding with the electronegative $\text{C}=\text{O}$ group on the polymer. The

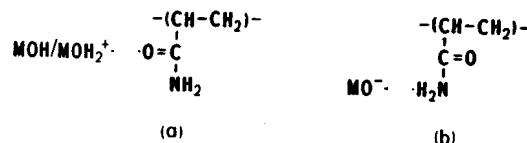
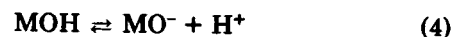


Figure 7. H bonding between PAM and oxide surface sites.

negative site, MO^- , being electronegative, is not favorable for bonding with the $\text{C}=\text{O}$, although at high pH, when the former is the predominant species, there is a possibility that it can bond with the weakly acidic NH_2 function, forming a weaker bond (Figure 7b). The importance of surface hydroxyl functions in H bonding has been further verified by adsorbing the polymer onto pure gold sol, the surface of which is not oxidized and therefore does not carry any hydroxyl groups; in this case, no adsorption of the polymer is detected.

Thus, the relative acidity/basicity of the chemical groups on the polymer with respect to the oxide surface groups results in a site preference in adsorption which is manifested as a pH dependence. To test this, the site distribution of the oxide with pH is examined in relation to the pH dependence of the polymer adsorption.

Site Distributions on Oxides. Two methods are used to calculate charge distribution on an oxide surface. The first method, proposed by Parks and de Bruyn,²³ considers the hydrolysis of the dissolved metal species and the subsequent readsorption of the hydroxy-metal complexes on the surface. From the bulk species distribution diagram, and assuming that the ratios of the species at the interface are similar to those in the bulk, the surface species distribution can be estimated. Lai and Fuerstenau,²⁴ on the other hand, have argued against this model on the basis that oxides are quite insoluble. They proposed that the charging mechanism is due to the adsorption or desorption of H^+ by the surface hydroxyl to form MOH_2^+ or MO^- , respectively, represented by



From the law of mass action and the pzc of the oxide, a charge distribution function can be obtained. The two assumptions in this model are as follows: (i) the activity is taken to be the fraction of the species on the surface and (ii) the fraction of neutral sites at the point of zero charge is an arbitrary value.

The site distribution curves for Fe_2O_3 obtained by using the models of Parks and de Bruyn and of Lai and Fuerstenau are plotted in Figure 8. The sum of the positive and the neutral sites is represented in boldface. The pH dependence of the adsorption density at a constant residual polymer concentration is also plotted in the same figure. It is clear from this figure that the sum of the positive and neutral sites gives a better correlation with adsorption density than either of the two alone: this supports the postulate that both the positive and neutral groups on the Fe_2O_3 are the adsorption sites. The same correlations are also obtained for Cr_2O_3 , Al_2O_3 , and TiO_2 (Figures 9–11), showing that this hypothesis holds true also for other oxides.

From the above correlations, it appears that the positive and the neutral surface groups are the preferred adsorption sites and that H bonding can be charge or pH dependent due to the relative acidity and basicity of the surface

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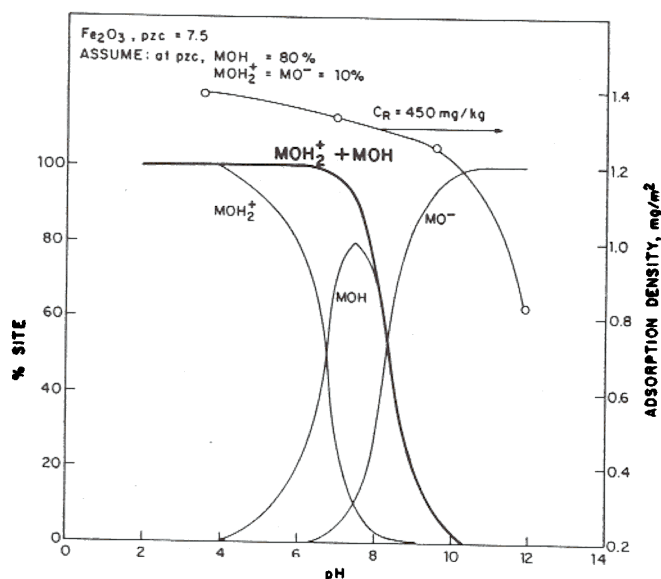
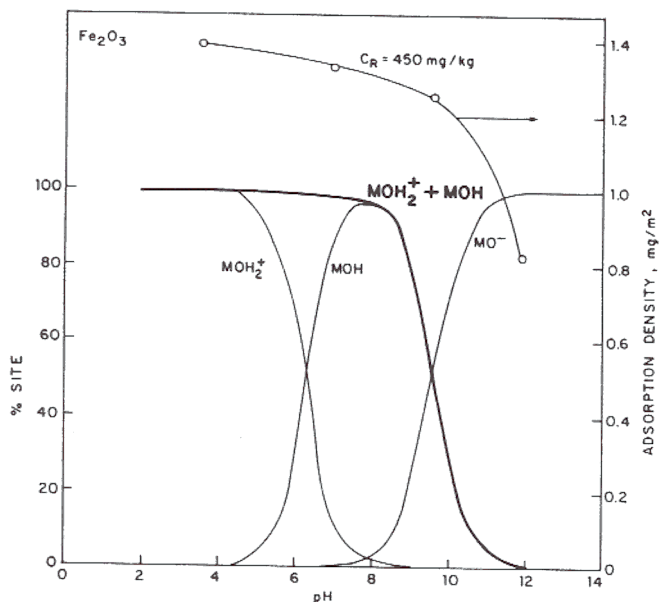


Figure 8. (a, Top) Comparison of PAM adsorption on Fe_2O_3 with surface site distributions calculated by using the model of Parks and de Bruyn. (b, Bottom) Comparison of PAM adsorption on Fe_2O_3 with surface site distributions calculated by using the model of Lai and Fuerstenau.

groups with respect to the polymer functional groups.

This being the case, can the differences in adsorption densities between oxides (see Figure 2) be attributed solely to the variations in surface charge densities? One way to isolate the extent of the charge effect is to plot the adsorption densities as a function of the difference, $\text{pH} - \text{pzc}$. Figure 12 shows such a plot for Fe_2O_3 , Cr_2O_3 , Al_2O_3 , and TiO_2 . In this figure, for a fixed value of $\text{pH} - \text{pzc}$, all the oxides represented should ideally have the same surface potential since according to the Nernstian equation²⁵

$$\psi_0 = -0.059(\text{pH} - \text{pzc}) \quad (5)$$

Hence, if charge were the only governing factor in adsorption, all the curves for the oxides should be superimposable. But this is not the case; clearly, charge effects alone cannot account for the characteristic adsorption densities for the oxides. It is possible that the oxides are

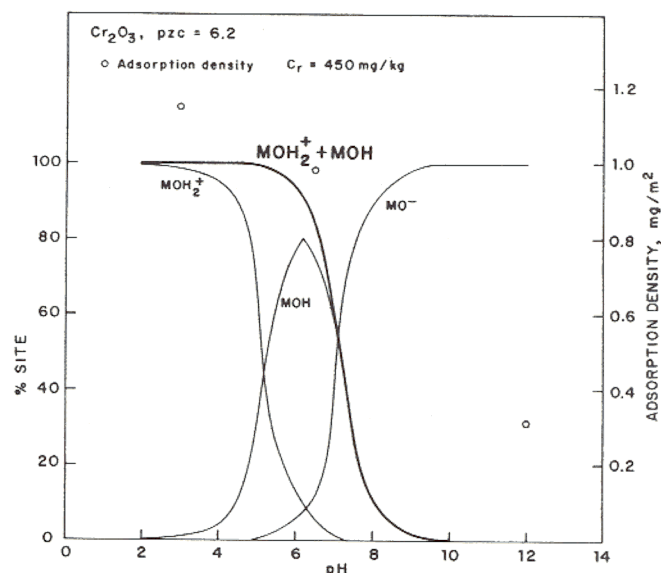


Figure 9. Comparison of PAM adsorption on Cr_2O_3 with surface site distributions.

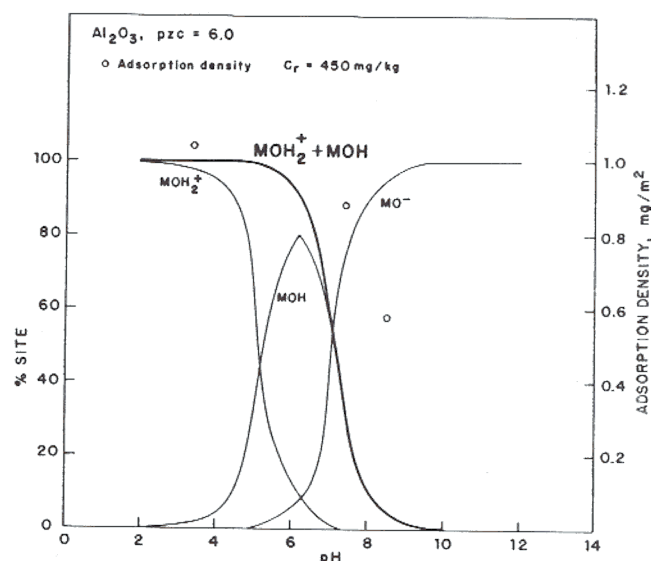
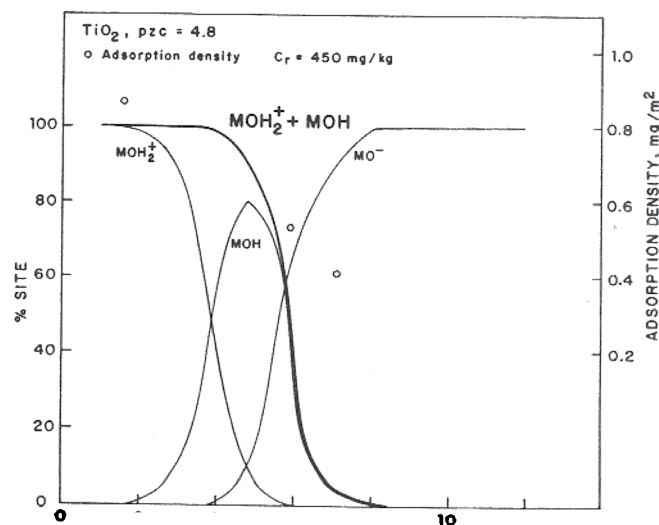


Figure 10. Comparison of PAM adsorption on Al_2O_3 with surface site distributions.



(25) De Bruyn, P. L.; Agar, G. E. In *Froth Flotation; 50th Anniversary Vol.*; Fuerstenau, D. W., Ed.; AIME: New York, 1962; p 91.

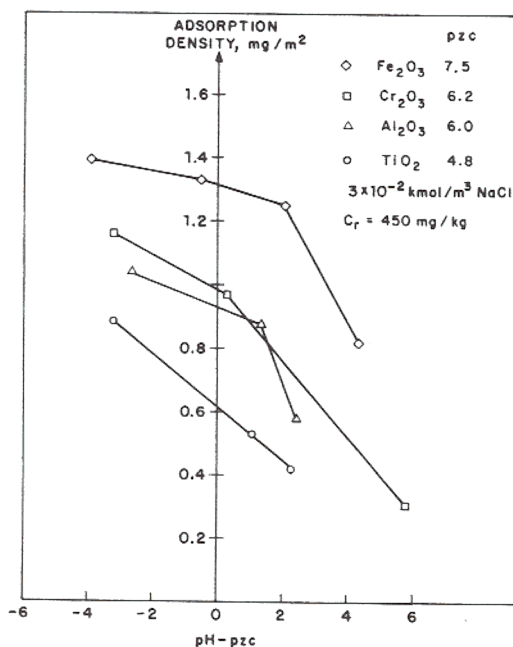


Figure 12. Adsorption densities of PAM on Fe_2O_3 , Cr_2O_3 , Al_2O_3 , and TiO_2 versus $(\text{pH} - \text{pzc})$.

Table III. Solvation Energies of Oxide Cations

cation	$r_{\text{ion}}, \text{\AA}^{27}$	$-\Delta G_{\text{solv}} \times 10^{-3}, \text{kJ/mol}$
		1.8
		1.8
		1.9
		3.2
		3.2
		3.5

non-Nernstian in behavior, possibly due to solvation effects.

Therefore, another factor considered to account for the differences in adsorption capacities of the oxides is solvation energy since, due to the polar nature of the system, the solvation factor can play an important role in the overall adsorption process.

Effects of Cation Solvation. The extent of solvation of the surface species on a particle is an important consideration because it reflects the affinity of the solvent for the solid, which in turn affects the surface-adsorbate interaction. Minerals undergo various degrees of interaction with the solvent depending on the nature of the surface species. The general equation for the calculation of solvation energy for a charge species according to the Born model is²⁶

$$\Delta G_{\text{solv}} = -\frac{(ze)^2 N}{8\pi(r_{\text{ion}} + 2r_w)\epsilon_0} (1 - 1/\epsilon_s) \quad (6)$$

In this expression, an ion with a bound layer of primary water is taken from vacuum to a medium of dielectric constant, ϵ_s . However, for a mineral particle, calculation of hydration energy is not straightforward, because it is the surface ions that undergo solvation; the appropriate values for the charges and radii of these bound surface ions are ambiguous. But it is possible that the extent of solvation of the dissolved oxide cations in the bulk solution will reflect that of the corresponding oxide particle surface. The calculated values of solvation in water of these cations obtained by using Born's equation are given in Table III.

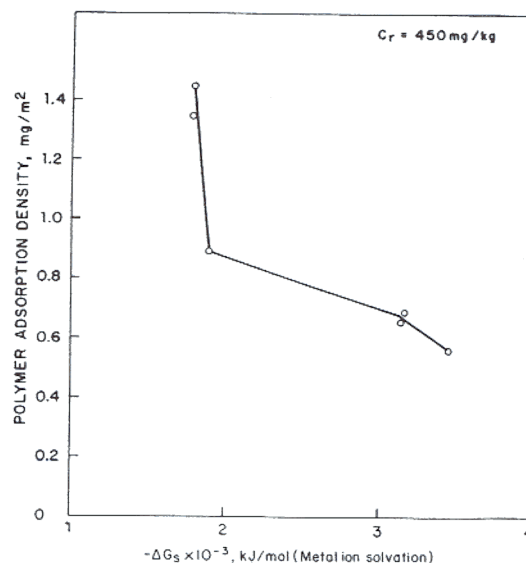


Figure 13. Effects of oxide cation solvation on PAM adsorption on oxides.

From Table III, it can be seen that as the solvation energy increases from Fe^{3+} to Si^{4+} the polymer adsorption density on the corresponding oxide decreases (see Figure 13). Such an inverse relation is comprehensible since a high degree of solvation implies a strong interaction of the solid and the solvent, and the affinity of the polymer for the surface is consequently decreased or hindered by the solvation layer on the solid surface.

The above calculations consider the solvation of free unhydroxylated cations only. Since the mineral is in equilibrium with several dissolved species such as Me^{3+} , $\text{Me}(\text{OH})^{2+}$, $\text{Me}(\text{OH})_2^+$, and $\text{Me}(\text{OH})_4^-$, a more complete calculation can be carried out by taking all these species into account. For each species, the solvation energy is estimated by using the Born equation and multiplied by the fraction of the species present in the solution at a given pH (evaluated from the species distribution diagram). Hence, at each pH, the total solvation is the sum of solvation of all the major dissolved species present. Note that although solvation of the dissolved species in solution is not equivalent to the solvation of the oxide surface, the dissolved species, nevertheless, play a role in determining the surface properties, as proposed by Parks and de Bruyn.²³ According to their hypothesis, the charge distribution on an oxide surface is due to the hydrolysis of dissolved metal species and the subsequent readsorption of the hydroxy-metal complex on the surface. Therefore, following the above hypothesis, the solvation behavior of dissolved species can reflect that of the oxide surface.

The results of total solvation of the dissolved oxide species calculated as a function of pH are given in Figure 14. For each oxide, the energy of solvation goes through a minimum as a function of pH. This means that considering the contribution of solvation energy alone, adsorption should go through a maximum. But from the earlier discussion, it has been shown that surface charge plays an important role and that polymer adsorption correlates with surface site distribution as a function of pH. Therefore, for an individual oxide, the predominant force responsible for polymer adsorption is H bonding, and the resultant pH dependence of adsorption is due to the site dependence of H bonding. Between various oxides,

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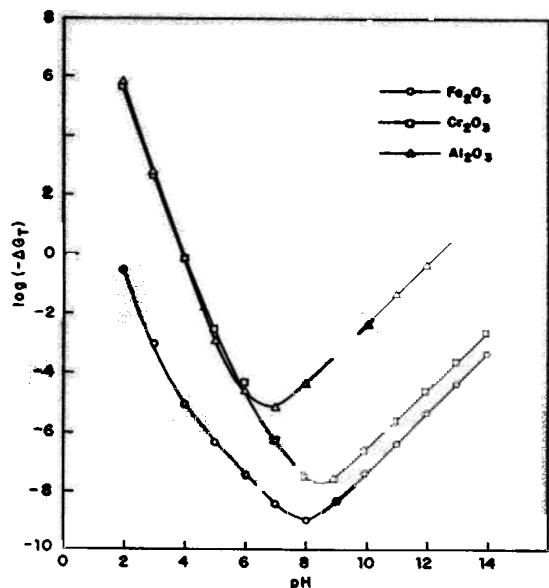


Figure 14. Total solvation of predominant oxide species in solution as a function of pH.

however, the degree of mineral-solvent interaction can explain the differences in polymer adsorption on these oxides. This is shown in Figure 14, where the energy of solvation increases from Fe_2O_3 to Cr_2O_3 to Al_2O_3 , a trend which corresponds to the inverse of that for polymer adsorption; this is attributed to competition between solid-solvent and solid-polymer interactions.

Thus, the present study has shown that, for the adsorption of nonionic polyacrylamide on oxides, pH is an important parameter due to the dependence of H bonding on the nature of the surface sites and that the extent of mineral solvation constitutes an additional factor which

determines the differences in polymer adsorption between various oxides.

Conclusions

The adsorption of nonionic polyacrylamide on oxide minerals is strongly dependent on the solution pH, and a correlation is found between the adsorption density and the pzc of the oxide. This indicates that even though the polymer is essentially nonionic the surface charge of the oxide plays an important role in the adsorption process.

The major driving force controlling polymer adsorption, H bonding, is proposed to take place between the electronegative C=O group on the polyacrylamide and the proton-donating oxide surface hydroxyls, the positive MOH_2^+ and the neutral MOH. The negative site, MO^- , being electronegative, is not as favorable to interact with the polymer. A correlation is obtained for the adsorption density and the distribution of the positive and neutral sites as a function of pH. The site preference of the polymer is thus explained in terms of the relative acidity/basicity of the polymer functional groups with respect to the oxide surface groups.

Another driving force that influences adsorption is solvation. The solvation energies of the ionic species from the oxides estimated by using the Born equation are found to follow an inverse relationship with the adsorption densities of the polymer on the oxides. This is attributed to competition between oxide-solvent and oxide-polymer interactions.

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Registry No. Fe_2O_3 , 1309-37-1; Cr_2O_3 , 1308-38-9; TiO_2 , 13463-67-7; SnO_2 , 18282-10-5; SiO_2 , 7631-86-9; Al_2O_3 , 1344-28-1; polyacrylamide, 9003-05-8.

