ADSORPTION OF HYDROLYZED POLYACRYLONITRILE ON KAOLINITE[1]

by

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ABSTRACT

Adsorption experiments were conducted by mixing homoionic kaolinite and C^{14}-labeled hydrolyzed polyacrylonitrile (HPAN) in water and solutions of electrolytes. Langmuir type adsorption isotherms resulted. Exchange cations on kaolinite increased adsorption in approximately the same order as such cations reduce zeta potential, *i.e.* $Th^{4+} > Ca^{2+} > Ba^{2+} > H^+ > NH_4^+ > K^+ > Na^+$. The anomalous increase in adsorption in the presence of polyvalent exchange cations suggested adsorption at the site of base exchange salt formation. Sorbed anions increased adsorption of HPAN in the order of electronegativity, *i.e.* $F^- > OH^- > H_2PO_4^- > Cl^- > CH_3COO^- > NO_3^-$.

An increase in the concentration of electrolyte and acidity of the adsorbate medium increased adsorption of HPAN. This effect was apparently due to the reduction of electrostatic repulsion between HPAN and kaolinite and a reduction in size of the polymer coil. Divalent cations, especially the transition metals capable of being complexed by HPAN, were more effective than univalent cations. Dissolution of the clay lattice caused desorption of HPAN.

HPAN adsorption reduced the intensity of the OH and O–Al–OH bands in infrared absorption spectra of the kaolinite. Preadsorption of aurintricarboxylic acid blocked adsorption of HPAN, suggesting that "positive spots" due to exposed lattice aluminum on edges of the clay platelets were adsorption sites.

INTRODUCTION

Synthetic polyelectrolytes have been used successfully to stabilize drilling muds and soil aggregates (Symposium on Soil Conditioners, 1952; Quastel, 1954), and to flocculate solids in extractive metallurgical operations (Wadsworth and Cutler, 1956). Adsorption of the polyelectrolyte and subsequent bridging between solid particles is thought to be necessary before stabilization of floccules and aggregates can occur (Ruehrwein and Ward, 1952). Hydrogen bonding (Michaels, 1954; Montgomery and Hibbard, 1955;

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Emerson, 1956), displacement of water of hydration (M. E. Wadsworth and A. C. Peck, private communication, 1958) and ionic interaction with (001) edges of clay (Street, 1959; Packter, 1957; Warkentin and Miller, 1958) have been proposed as bonding mechanisms, but the evidence in support of these theories has been of indirect nature. The effect of exchange cations and anions and solution electrolytes on adsorption of synthetic polyelectrolytes on clays has not been adequately evaluated (Bergmann and Fiedler, 1956).

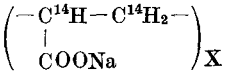
The purpose of this study was to determine the effect of polymer configuration and structure of the clay surface on the adsorption of hydrolyzed polyacrylonitrile (HPAN) on kaolinite. The tracer method using C^{14}-labeled HPAN was used to circumvent difficulties of analytical methods involving coprecipitation with counter polyelectrolytes (Michaels and Morelos, 1955). Some of the results reported herein have appeared elsewhere (Mortensen, 1957; Mortensen, 1959).

EXPERIMENTAL PROCEDURE

Adsorption

Preparation of kaolinite.—The homoionic saturation of kaolinite[1] (Vanderbilt Peerless no. 1—used as received) with various cations and anions was accomplished by repeated suspension in 0.5 M solutions of their chloride or sodium salts. The clay was then filtered, washed with distilled water until free of chloride or sodium ions, and oven-dried. The kaolinite lattice apparently is quite stable to leaching with chloride salts, but acids, phosphates, hydroxides and fluorides affect surface structure by dissolution of the clay lattice (Low and Black, 1948; Mukherjee, Chatterjee and Ray, 1948; Romo and Roy, 1957).

Hydrolyzed polyacrylonitrile.—The HPAN used in this study was commercial material and consisted essentially of sodium polyacrylate. Properties of the labeled HPAN are shown below (Mortensen and Martin, 1954):



$$\left(\begin{array}{l} -\mathrm{C^{14}H}-\mathrm{C^{14}H_2}- \\ \;\,| \\ \mathrm{COONa} \end{array}\right)_{\mathrm{X}}$$

specific isotopic content, 0.10 percent,
specific activity, 1.9 μc/mg,
molecular weight (approx.), 60,000.

[1] Particle size = 81 percent 5 μ or smaller, 56 percent 2 μ or smaller, 13 percent 0.2 μ or smaller; ethylene glycol retention (method of Martin, 1955) = 10.1 mg/g (≈32.6 m^2/g); characteristic DTA, IR and X-ray kaolinite patterns.

Adsorption experiments.—Adsorption experiments were conducted by mixing 500 mg homoionic clay and the required quantity of HPAN containing 0.2 μc of C^{14}-labeled HPAN in 10 ml distilled water, solutions of electrolytes or buffer solutions. In some experiments, the clay was premixed with 5 ml of electrolyte solution for 20 hr prior to the addition of 5 ml HPAN in distilled water. Separate triplicates of clay and adsorbate medium for each adsorption period were placed in screw-cap vials, clamped to a Plexiglas wheel and turned at 10–12 rpm in a water bath thermostatically controlled at 30 °C. After the prescribed time of mixing, or until steady state adsorption had occurred (6 hr), the suspensions were poured into Lucite tubes and centrifuged at 12,000 rpm. Aliquots of the supernatant liquid were placed in aluminum planchets, dried under a heat lamp and assayed for remaining radioactivity with a preflush gas flow counter. Labeled HPAN not thus detected was assumed to be adsorbed on the kaolinite.

Infrared Absorption Spectra

Following some of the adsorption experiments, unadsorbed HPAN was washed from the clay in the centrifuge tubes with distilled water. The clay was then dried over $MgClO_4$ *in vacuo*, ground with KBr at 0.16 percent concentration with a mortar and pestle and pressed into discs. Infrared absorption spectra were obtained using a Perkin–Elmer model 21 spectrophotometer with a NaCl prism.

RESULTS AND DISCUSSION

The data indicated that steady state adsorption generally occurred in about 4 hr. A plot of the log of the time of mixing *vs.* mg HPAN adsorbed/mg HPAN in solution indicated that adsorption occurred as a simple uni-step process. Adsorption equilibrium in the presence of polyvalent exchange cations and "adsorbable" anions in solution was not attained in mixing times used in these experiments.

The effects of the exchange cation on increasing adsorption of HPAN (Fig. 1) was in the order $Th^{4+} > Ca^{2+} > Ba^{2+} > H^+ > NH_4^+ > K^+ > Na^+$. This order is similar to the effect of such cations on the reduction of zeta potential of clays (Jenny and Reitmeier, 1935; Tuorila, 1928). Since both the clay and HPAN are essentially polyanionic, a reduction in the magnitude of the potential barrier should increase the possibility of approach and attachment of an HPAN molecule to an adsorption site on the clay. The displacement of H^+ from its usual terminal position in the lyotropic series by polyvalent cations suggests the adsorption of HPAN by bridging through coulombic linkages involving ionized carboxyl groups (Clay—Ca—OOCR) (Marbol and Weyl, 1947; Peterson, 1948) and base exchange salts (Bower and Truog, 1941; Engabaly and Jenny, 1943).

Fig. 1 (dashed line) also indicates that sodium gegenions of the HPAN displaced exchange cations on the clay. Radioactive thorium in the supernatant from Th-kaolinite was determined and accounted for in separate adsorption experiments using inactive HPAN. Such displaced cations

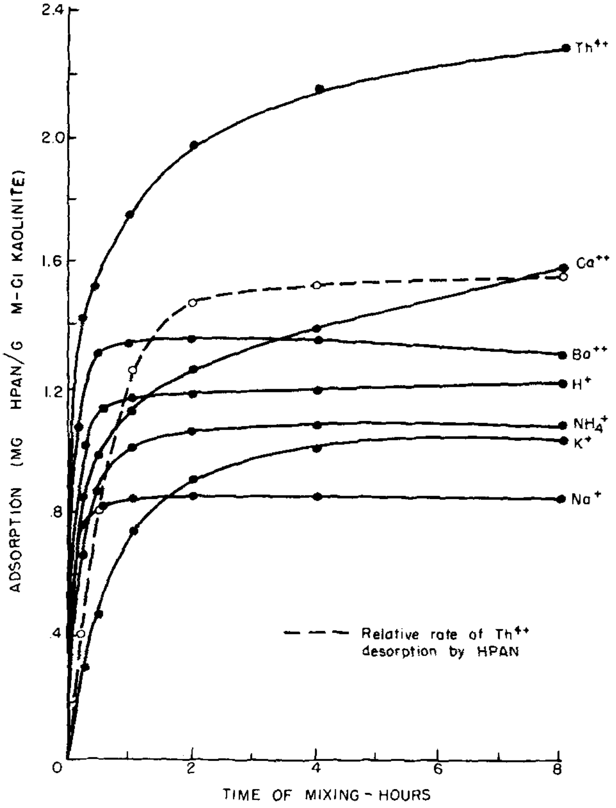


FIGURE 1.—Effect of exchange cation on the adsorption of HPAN on kaolinite ($C = 5$ mg/g).

also could affect adsorption by altering the configuration of the polymer coil.

The effect of the "sorbed" anion in increasing the adsorption of HPAN was in the order: $F^- > OH^- > H_2PO_4^- > Cl^- > CH_3COO^- > NO_3^- >$ HPAN (Fig. 2). The preparative saturation procedure apparently created differences in the anion surface of the kaolinite. Anion exchange on clays has been demonstrated (Dean and Rubins, 1947; McAuliffe *et al.*, 1948), but the exchange in some instances is accompanied by transformations in the crystal lattice (Low and Black, 1948; Romo and Roy, 1957; Schofield, 1940). Univalent anions have little effect on zeta potential of clay (Tuorila, 1928), but their marked effect on properties of colloidal systems has been ascribed to differences in electric field strength (Voet, 1937).

There was little exchange of adsorbed HPAN for HPAN in solution.

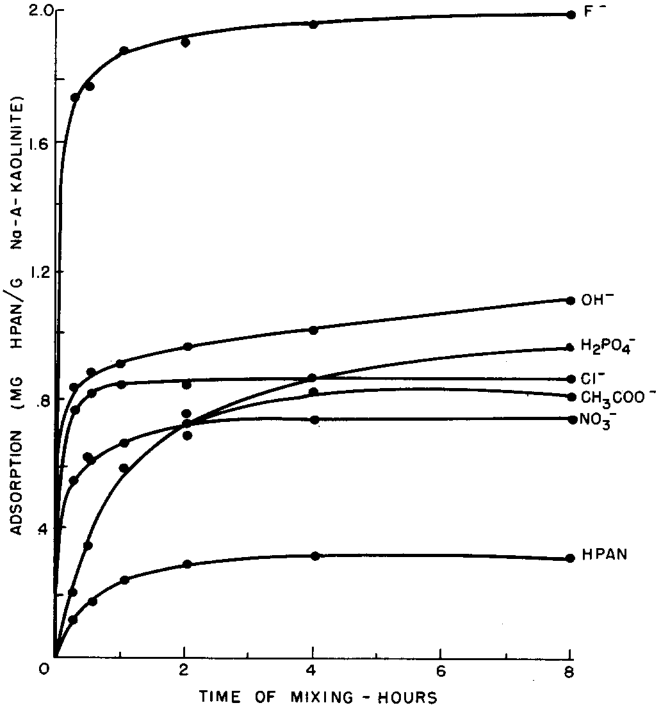


FIGURE 2.—Effect of sorbed anion on the adsorption of HPAN on kaolinite ($C = 5$ mg/g).

Once HPAN becomes "fixed" on a clay surface by a drying cycle (Mortensen and Martin, 1956) there is apparently little exchange for HPAN in solution. Adsorbed HPAN no doubt increased the zeta potential of the clay and thus reduced exchange. HPAN effectively replaces "sorbed" $H_2PO_4^-$, however. The anion exchange capacity (method of Rubins and Dean, 1947) of the kaolinite using HPAN as the replacement solution was 4.4 meq/100 g. A fluoride replacement solution gave a value of 4.7 meq/100 g.

Adsorption of HPAN from solutions of electrolytes increased with an increase in the concentration of electrolyte (Figs. 3, 4, 5). These results can be explained by the effect of salts in reducing zeta potential of the kaolinite and the charge and size of the HPAN polymer. The increased concentration of counterions increased the shielding of negatively charged groups on the HPAN chains and reduced their size and configuration to that of normal random coils (Flory and Osterheld, 1954; Katchalsky, 1951). Closer packing and more extensive adsorption of HPAN on the kaolinite surface would thus be made possible.

Figs. 4 and 5 indicate that 2 : 1 electrolytes were more effective than 1 : 1 electrolytes in increasing adsorption of HPAN. The order of cation effectiveness at 0.003 N concentration ($Mg^{2+} > Ca^{2+} > Ba^{2+}$) was similar to that reported for reduction in zeta potential of kaolinite (Tuorila, 1928)

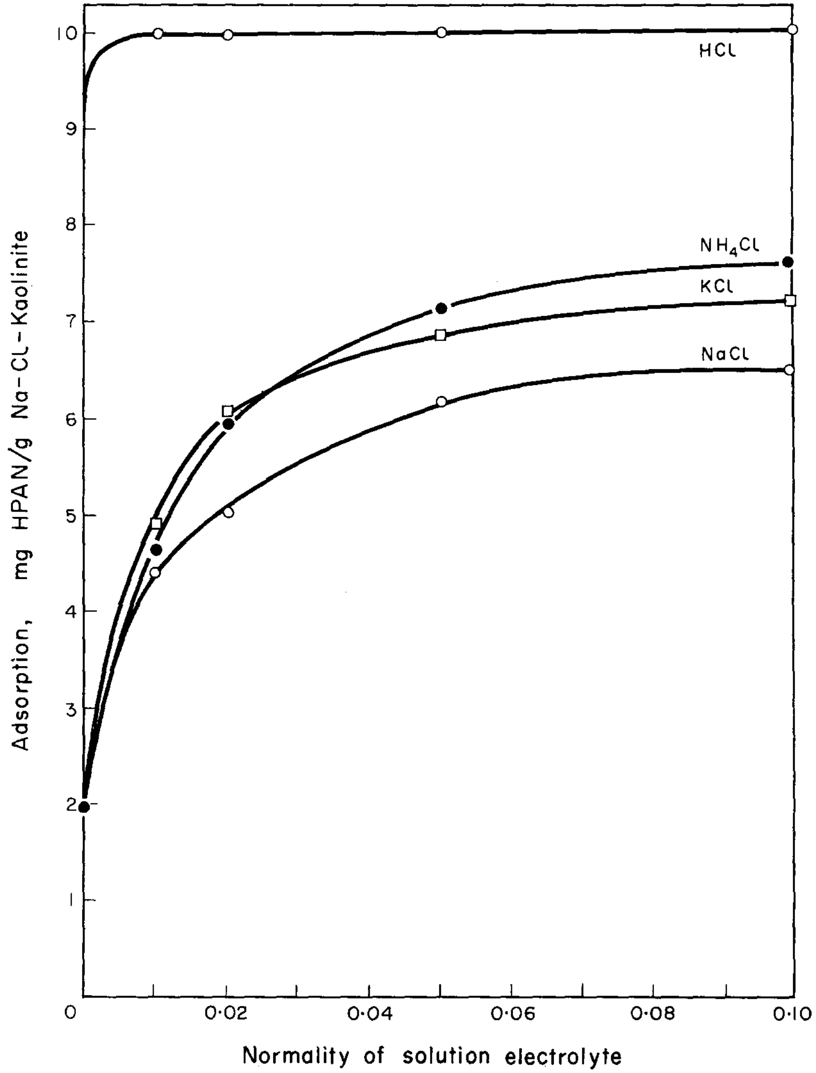


FIGURE 3.—Effect of 1 : 1 electrolytes on adsorption of HPAN on Na-Cl-kaolinite ($C = 10$ mg/g).

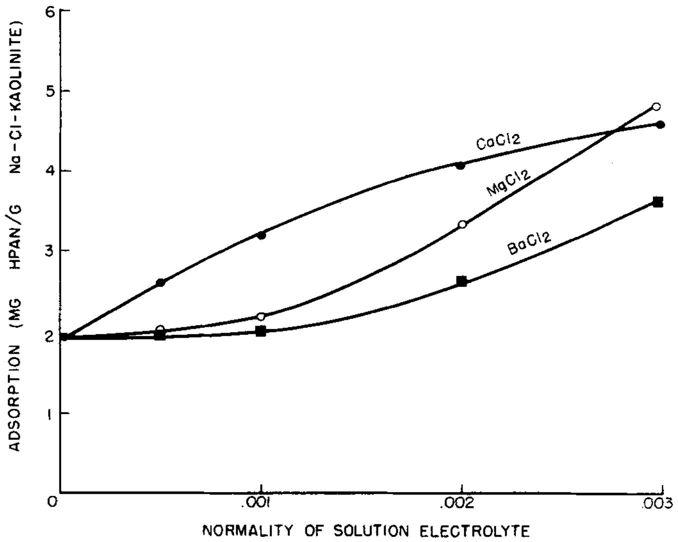


FIGURE 4.—Effect of 2:1 electrolytes on adsorption of HPAN on Na-Cl-kaolinite ($C = 10$ mg/g).

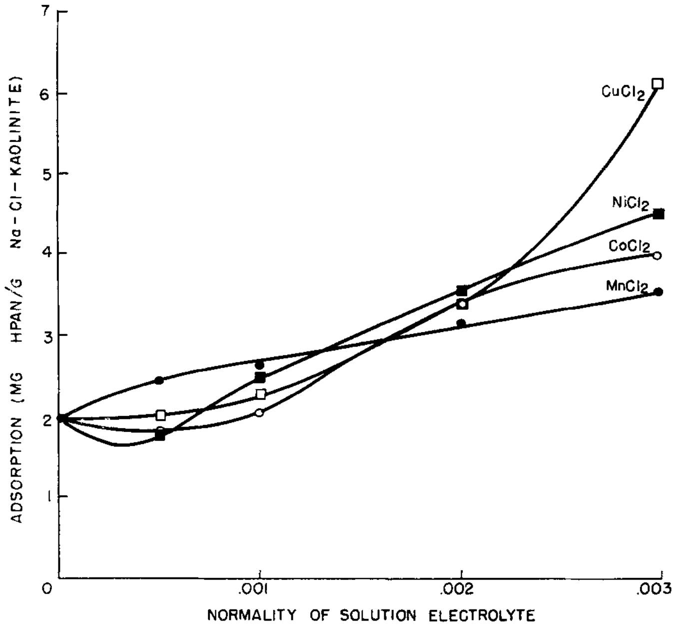


FIGURE 5.—Effect of 2:1 complexable electrolytes on adsorption of HPAN on Na-Cl-kaolinite ($C = 10$ mg/g).

and viscosity of polyacrylate solutions (Markovitz and Kimball, 1950). The shape of the adsorption isotherms was considerably different from that of 1 : 1 electrolytes, suggesting a bridging of divalent cations between the kaolinite and HPAN.

The effect of complexable electrolytes on the adsorption of HPAN ($Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$, Fig. 5) was identical to the order reported (Gregor, Luttinger and Loebl, 1955; Irving and Williams, 1948) for stability of metal complexes. Intramolecular complexing of these metals reduced the charge and size of the HPAN chains, leading to increased adsorption. HPAN-copper complexes developed the blue color characteristic of Cu-polyelectrolyte complexes (Wall and Gill, 1954). Complexing of these metals may also have increased the polarity of the C—H group in the HPAN molecule leading to adsorption by an ion-dipole mechanism ($C^- — H^+ \cdots O^-$) (Bradley, 1945; Taylor and Rutzler, 1958).

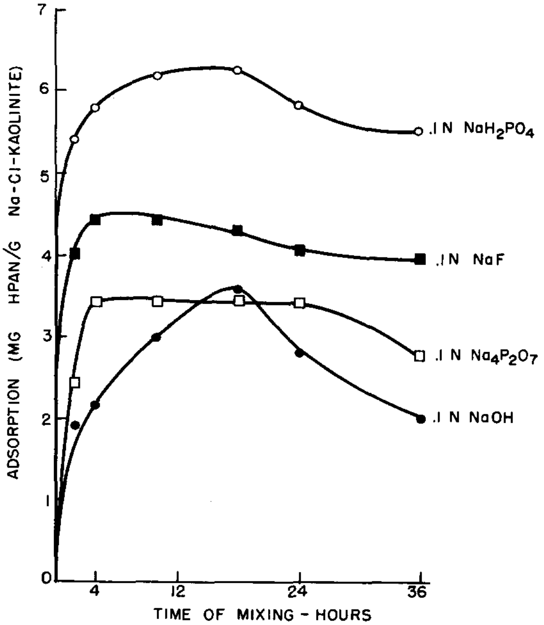


FIGURE 6.—Effect of sorbable anions in solution on adsorption of HPAN on Na-Cl-kaolinite ($C = 10$ mg/g).

Solutions of sodium salts of anions not extensively adsorbed by clay (Cl^-, CH_3COO^-, $Fe(CN)_6^{4-}$, SO_4^{2-}) had little effect on adsorption of HPAN. Fig. 6 shows that anions that are "sorbed" or attack the clay lattice had considerable effect ($OH^- > P_2O_7^{4-} > F^- > H_2PO_4^-$) on the adsorption of HPAN on Na-Cl-kaolinite. Dissolution of the clay lattice probably took place (Grim, 1953, pp. 295–303) during the later stages of the mixing period and resulted in desorption of HPAN. Dissolution of the clay lattice apparently is preceded by the complexing of lattice aluminum (Hofmann *et al.*, 1956; Low and Black, 1948). Competitive zeta potential (Holmes and Toth, 1957; von Wazer and Besmertnuk, 1950) and pH effects also could have reduced adsorption in the presence of adsorbable anions.

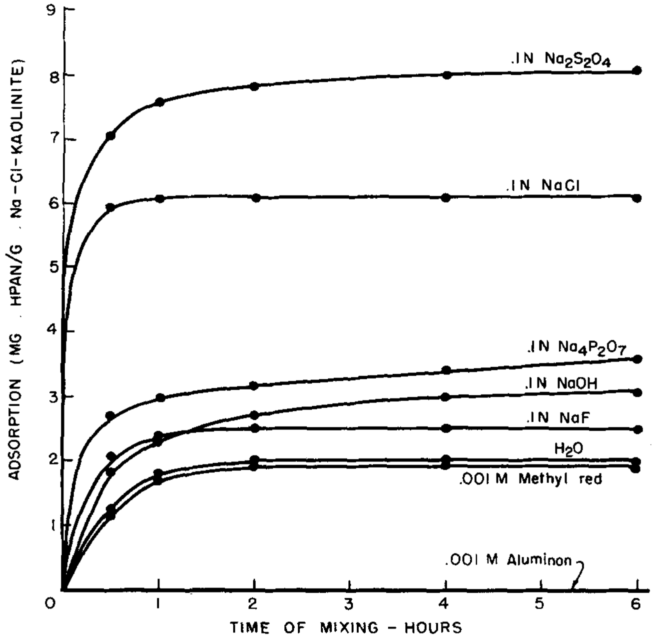


FIGURE 7.—Effect of pretreatment on adsorption of HPAN by Na-Cl-kaolinite ($C = 10$ mg/g).

Desorption of HPAN did not take place when solutions of "sorbable" anions were premixed with kaolinite (Fig. 7). Structural alterations of the clay surface probably occurred before the HPAN was added to the adsorbent medium. Premixing with 0.1 N NaCl did not alter adsorption from that of the HPAN and NaCl mixture. The increased adsorption in the presence of sodium dithionite may have been due to the partial dissolution (Deb, 1950) of the amorphous Beilby layer (van der Marel, 1960) surrounding the clay particles. Removal of this layer could have exposed additional adsorption sites.

Fig. 7 shows that adsorption of HPAN was completely inhibited when Na-Cl-kaolinite was premixed with a 0.001 N solution of the NH_4-salt of aurintricarboxylic acid (Aluminon). Aluminon probably complexed exposed aluminum on the edges of the kaolinite platelets (Russell and Low,

1954) and prevented adsorption of HPAN. Some HPAN was adsorbed (0.53 mg/g in 6 hr) after Ca-Cl-kaolinite had been premixed with Aluminon, indicating that Ca formed a bridge between the kaolinite and HPAN. Premixing Na-Cl-kaolinite with aqueous methyl red or using a methyl red–kaolinite prepared from benzene solution (Alexander, Broge and Iler, 1956; Shapiro and Kolthoff, 1950) did not affect adsorption of HPAN. Methyl red is adsorbed by silanol groups on the clay surface (Alexander, Broge and Iler, 1956). The kaolinite remained dyed during the mixing process, but some hydrolysis and desorption of the methyl red probably occurred. It appears, however, that silanol groups are not involved in the adsorption of HPAN on kaolinite. These data suggest that HPAN is adsorbed on the edges of kaolinite platelets on positively charged sites (Ford, Loomis and Fidiam, 1940; Schofield, 1940) of exposed lattice aluminum. Rheological (Street, 1959; Packter, 1957), swelling (Emerson, 1956; Warkentin and Miller, 1958), and surface (Beischer, 1953; Thiessen, 1942) studies also suggest that polyanions are adsorbed on the edges of clay platelets.

That pH of the adsorbate medium markedly affected adsorption of HPAN on kaolinite can be seen in Fig. 8. The increase in adsorption as acidity increased was probably due to the effect of hydrogen ions in reducing zeta potential and rendering the clay more electropositive (Russell, 1950, p. 94), reducing the size of the HPAN coil by intramolecular hydrogen bonding (Silberberg, Eliassof and Katchalsky, 1957), and the creation of a $H^+ \cdot Al^{3+}$ surface on the clay (Mukherjee, Chatterjee and Ray, 1948), the latter effect increasing adsorption by a bridging mechanism. Increasing basicity could have reduced adsorption by increasing electronegativity of the kaolinite (Russell, 1950, p. 94), by increasing electronegativity and size of the polymer coil by ionization effects (Katchalsky, 1951), by competition for adsorption sites (Dean and Rubins, 1947) and by dissolution of the clay lattice (Grim, 1953 pp. 295–303). Dissolution of the clay lattice takes place in both acid and basic media, but aluminate anions are formed by bases, aluminum cations by acids. Adsorption of HPAN in the presence of various exchange ions no doubt was influenced by pH since equilibrium pH values varied from 6.0 to 8.4.

Buffer species had less effect on total adsorption than pH, but adsorption isotherms in the presence of phosphate and borate were of peculiar shape. The effect of phosphate on kaolinite structure has been mentioned above. Borate may have influenced adsorption by partial dissolution of the Beilby layer surrounding the kaolinite platelets (Gibb, Ritchie and Sharpe, 1953; van der Marel, 1960).

An increase in adsorption does not necessarily mean, however, that increased flocculation and aggregation of particles will occur. Bridging of particles by polyelectrolyte chains (Ruehrwein and Ward, 1952) is necessary before flocculation can occur. In additon to ordinary dispersion factors, high concentrations of solution electrolytes reduce the size of the HPAN coil and prevent extensive "bridging" between solid particles. Concentrations of polyelectrolyte above maximum adsorption cause dispersion.

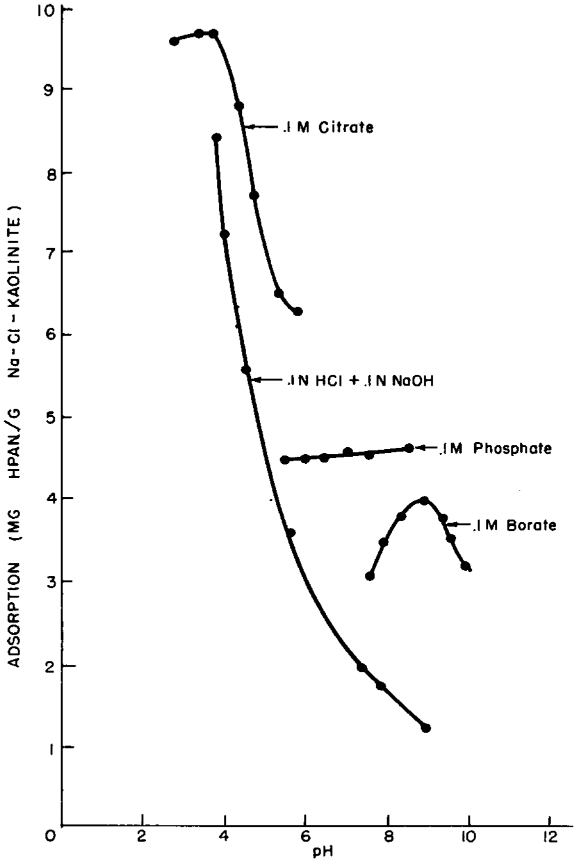


FIGURE 8.—Effect of pH and buffer species on adsorption of HPAN on Na-Cl-kaolinite ($C = 10$ mg/g).

Conformity of the adsorption data to the Langmuir equation (Fig. 9) suggests that HPAN was adsorbed as a monolayer on active sites of the kaolinite and that there was no interaction between adsorbed molecules. An estimate of maximum binding was made by the use of Klotz's (1953) equations. Where the equivalent weight of HPAN is the molecular weight of the monomer unit, maximum adsorption from distilled water solutions of HPAN was 1.5 meq/100 g for Na-Cl-kaolinite and 2.6 meq/100 g for H-Cl-kaolinite. Because of the effects of exchange and solution ions on adsorption, estimates of maximum binding are valid only for the conditions of the particular experiment. Simha, Frisch and Eirich (1953) have shown that only a fraction of the active groups of a polymer chain can be expected to be anchored to the adsorbent. This factor could account for high adsorption values obtained in some of the experiments. Stearic hindrance also could prevent complete saturation of all adsorption sites.

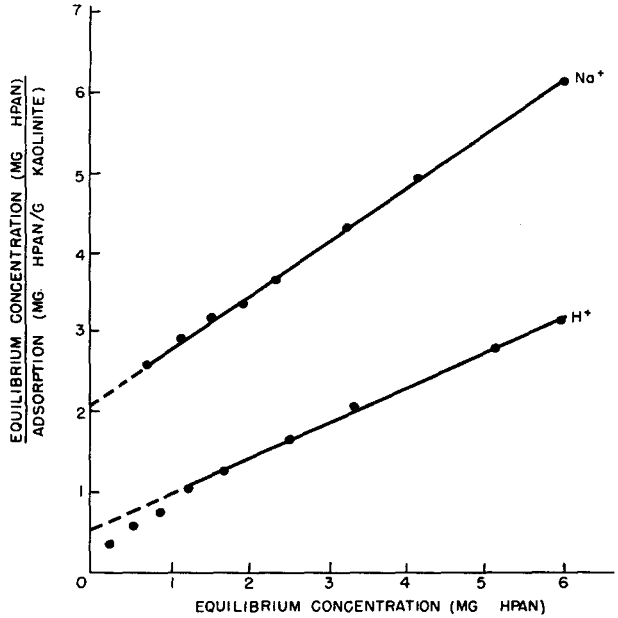


FIGURE 9.—Langmuir adsorption isotherms—HPAN adsorbed on H-Cl-kaolinite and Na-Cl-kaolinite.

Conformity of the data to the equations for maximum binding sites suggests that HPAN was bonded to a single type of adsorption site with no interaction between such sites. As indicated above, these sites are probably the positive spots on the edges of the clay platelets due to exposed lattice aluminum. Exchangeable polyvalent cations (base exchange salts) such as aluminum, calcium, etc., would provide similar sites for adsorption of HPAN by a bridging mechanism.

Further evidence that lattice aluminum is involved in the adsorption of HPAN can be seen in the infrared absorption spectra (Fig. 10). Adsorbed HPAN reduced the intensity of the O—Al—OH bands at 9.1 μ and 10.95 μ (Alder *et al.*, 1951). A slight reduction in intensity of the OH band at 2.65 μ suggests that carboxyl groups of the HPAN displaced OH^- associated with lattice aluminum. Spectra of kaolinite with adsorbed Aluminon were identical to that of kaolinite with adsorbed HPAN. Holmes and Toth (1957) reported a similar reduction, but French *et al.* (1954), reported an increase in intensity of the OH band due to adsorption of polyelectrolytes on montmorillonite. Such results have been used for evidence in support of the hydrogen bonding theory of adsorption.

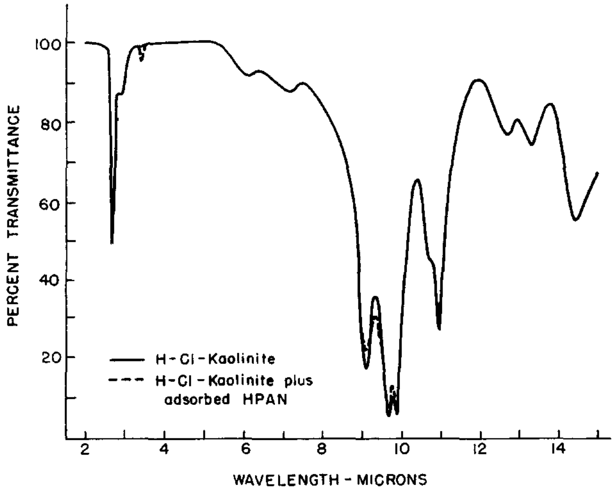


Figure 10.—Effect of adsorbed HPAN on infrared spectra of H-Cl-kaolinite.

CONCLUSIONS

Major factors affecting the adsorption of HPAN on kaolinite appear to be associated with electrostatic repulsive forces between adsorbent and adsorbate. Reduction of the zeta potential of the kaolinite and HPAN chains by exchange cations, solution electrolytes, and acidity increased adsorption. Ionic effects followed the usual lyotropic series indicative of reduction in zeta potential. The formation of base exchange salts on the clay surface by polyvalent cations increased adsorption by a bridging mechanism.

Dissolution of the clay lattice by reagents which complex aluminum reduced adsorption. Blocking of silanol groups did not affect adsorption, but blocking of exposed lattice aluminum completely inhibited adsorption of HPAN. Infrared absorption spectra also gave evidence that lattice aluminum was involved in adsorption.

HPAN apparently is adsorbed on kaolinite by the formation of ionic bonds between ionized carboxyl groups of HPAN and unsatisfied valence bonds of exposed lattice aluminum and base exchange salts on the kaolinite surface.

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