Adsorption Behavior of Poly(vinylpyrrolidone) Toward Fuller's Earth Suspensions

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ABSTRACT: The adsorption of poly(vinylpyrrolidone) (PVP) onto Fuller's earth surface was studied at fixed pH (4.2) and room temperature (27 $\pm$ 0.2°C). The kinetics of the adsorption process was monitored and various adsorption and kinetic parameters such as the adsorption coefficient, the rate constants for adsorption and desorption, the diffusion constant, and the penetration constant were evaluated. The effects of various experimental factors such as the pH and the presence of inorganic and organic anions or aliphatic alcohols were also studied on the adsorbed amounts of PVP. The role of temperature was also investigated and various thermodynamic parameters such as the standard Gibb's free energy, enthalpy, and entropy were also evaluated. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2122–2133, 2000

Key words: poly(vinylpyrrolidone); adsorption; Fuller's earth

INTRODUCTION

Water-soluble polymers find extensive use as flocculants in a number of industrial and technological dispersal systems.[1,2] When an aqueous solution of polymers is added to the particles, the dispersion stability of the particles is often influenced by the adsorbed amount and the conformation of the polymers adsorbed.[3] It is generally accepted that the adsorption of polymers on hydrophilic solid surfaces is predominantly governed by electrostatic attractions, H-bonding, and solvation forces. For charged polymers the electrostatic interaction is significant and parameters like the pH and ionic strength of the solution become the determining factors of adsorption.[4] If the surface and the polymer carry opposite charges, the electrostatic and H-bonding forces both favor the adsorption process. However, if they carry similar charges, then the adsorption is determined by the competition of attractive H-bonding forces and repulsive electrostatic attraction. For uncharged polymers only H-bonding and solvation forces, the latter of which always acts against adsorption, are considered to be important. In spite of this, adsorption of nonionic polymers on oxide minerals was found to be very pH dependent.[5]

Apart from the fact that the adsorption of ionic polymers is nicely reviewed[6] and the literature is richly documented[7] by the articles on polyelectrolyte adsorption, it is undoubtedly accepted that rather few investigations have been done on the adsorption of nonionic polymers.[8] Therefore, the main object of the present investigation was to study the adsorption of a nonionic polymer such as poly(vinylpyrrolidone) (PVP) on Fuller's earth surfaces in their aqueous suspensions. Fuller's earth is one of the most common bleaching clays and has a great number of applications as a potential adsorbent that selectively adsorbs impurities and coloring matter from oils and fats.[9]

EXPERIMENTAL

Materials

The PVP was obtained from Wilson Laboratories (India); its average molecular weight (about 12,000) was determined from viscosity measurements.[10] Fuller's earth was provided by Loba Chemie (India) and was used as received. The other chemicals employed were also AR grade.

Method

The adsorption experiments were carried out as described in our other communications.[11,12] In brief, 20 mL of PVP solution of a definite concentration containing 0.1 g of the adsorbent was shaken in a mechanical shaker (Toshniwal, India) at a fixed pH (4.2) and ionic strength (0.001M KNO_3) for 2 h, which had been predetermined as the equilibration time period for adsorption. After the adsorption experiment the suspensions were centrifuged and the residual concentration of PVP in the supernatants was determined colorimetrically using the iodine solution reagent prepared in KI.[13] The amount of the adsorbed PVP was calculated by the following mass balance equation:

$$\text{amount adsorbed (mg/g)} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 is the initial polymer solution concentration (mg/mL), C_e is the equilibrium polymer solution concentration (mg/mL), V is the volume (mL) of the polymer solution, and m is the weight (g) of the Fuller's earth.

Determination of Point of Zero Charge (PZC)

The PZC of the edge face of the Fuller's earth was determined by the potentiometric titration method. Fuller's earth suspensions (50 mL) containing 2 g of the clay and 1.0×10^{-3} mol/L of NaCl as the supporting electrolyte were titrated with 0.1N NaOH and the corresponding pHs and electromotive forces (emfs) were recorded by a digital pH meter (335, Systronics, India). The PZC was determined to be 7.0 from the graph plotted between the emf and pH as shown in Figure 1.

Kinetics of Adsorption

To monitor the progress of the adsorption process several identical sets were run simultaneously
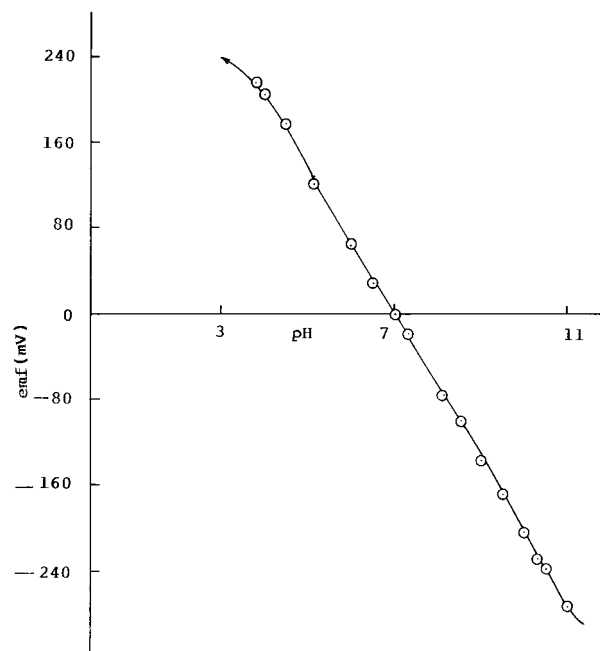

Figure 1 The determination of the point of zero charge (PZC) of the Fuller's earth by the pH titration method with 2.0 g Fuller's earth, [NaCl] = 1.0×10^{-3} mol/L (as a supporting electrolyte), and suspension volume = 50 mL.

and withdrawn one by one at definite time intervals. The amounts of adsorbed PVP in the respective supernatants were estimated as described above.

RESULTS AND DISCUSSION

Mode of PVP Adsorption

Before discussing the results it is essential to see how the PVP molecules adsorb on the Fuller's earth surfaces. Commercial grade Fuller's earth, irrespective of its origin, has 50–54% silica and 10–12% alumina and the remaining are other oxides.[14] The chief property of Fuller's earth is its adsorptive power. During the drying step the water is driven off, leaving particles full of submicroscopic pores. It is in these pores that the great area of the active adsorptive surface is probably developed. The normal limit of porosity is 60–70% and surface areas are 120–140 m^2/g. The pores have mean equivalent diameters of 190–200 Å. Because montmorillonite forms the major portion of this clay, we consider its crystal structure to explain the mode of the polymer adsorption. As far as the crystal structure of montmorillonite is
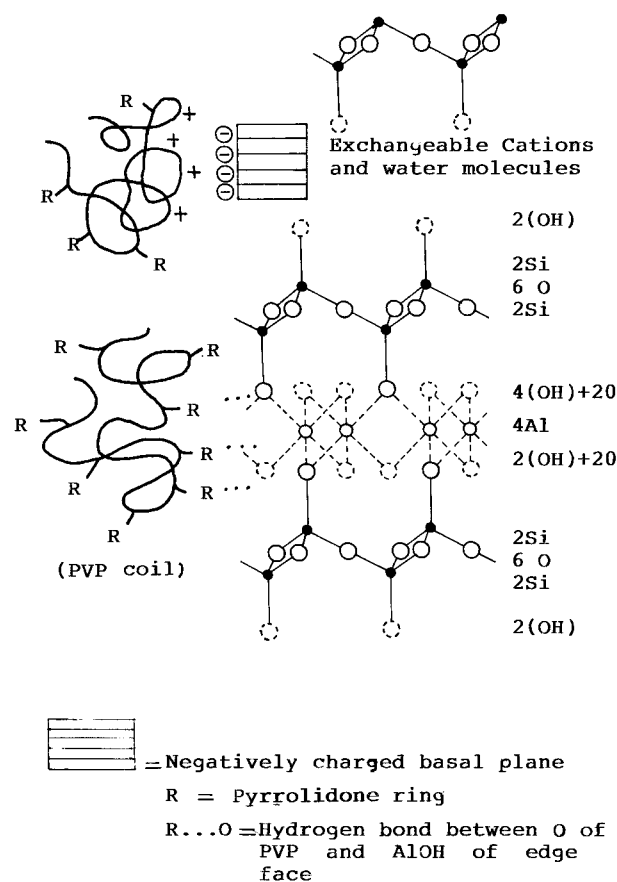
= Negatively charged basal plane

R = Pyrrolidone ring

R...O = Hydrogen bond between O of PVP and AlOH of edge face

Figure 2 A model proposed for the adsorption of PVP onto the Fuller's earth surfaces.

concerned (Fig. 2), it possesses a basal surface with a negative charge that arises from isomorphous charge substitution in the crystal lattice that is compensated by exchangeable cations from the external medium. Likewise, the edge face has a positive charge when the pH < 7, because Al—OH groups undergo protonation. Also, the edge face has a negative charge when the pH > 7.

PVP is a typical nonionic vinyl polymer and may be represented as

$$-(-CH_2-CH-)_n-, \quad R = \underset{R}{\overset{}{\underset{}{\bigcirc}}}$$
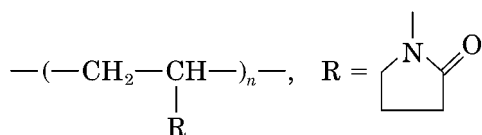
The adsorption of PVP on various oxides was studied in the recent past,[15] and the main adsorption forces are believed to be H bonding due to the oxygen atom of the pyrrolidone ring. In addition, because of the slightly positive charge of PVP,[16] electrostatic forces may also be operative. Thus,

in the present case the adsorption of PVP on Fuller's earth surfaces may occur due to the H-bonding and electrostatic forces as modeled in Figure 2.

Concentration Effect and Adsorption Isotherm

The effect of the change in the concentration of the PVP solution on the adsorbed amount was studied by varying the initial concentration of the polymer solution in a range of $4.18–20.9 \times 10^{-7}$ mol/L. As expected, the results implied that the adsorption gradually increases with increasing concentration of PVP in the solution. The reason for the observed increase is quite obvious because increasing the concentration of the PVP solution caused more PVP molecules to arrive at the interface and get adsorbed.

For a polymer molecule adsorbing on a solid surface, more quantitative and useful information is offered by the shape of the adsorption isotherm, which not only quantitatively relates the adsorbed amount to the adsorbate concentration but also provides clues about the orientation of the adsorbed molecules.[17,18] Such an isotherm in the present case is depicted in Figure 3, which was obtained by plotting the adsorbed amounts against the respective equilibrium concentration
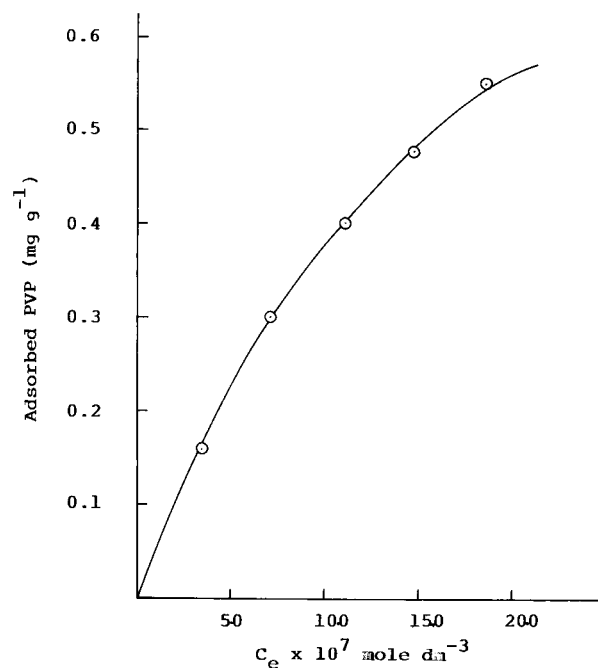

Figure 3 A plot showing the variation of the adsorbed amount (mg/g^1) with the equilibrium concentration of the PVP solution at a fixed pH of 4.2 and $[KNO_3]$ = $0.001M$ at $27 \pm 0.2°C$.

of polymer solutions. As revealed from Figure 3, the shape of the isotherm is Langmuirian in nature and no plateau region appears in this case. The reason for not going beyond a PVP concentration of 20.9×10^{-7} mol/L is that, while estimating PVP colorimetrically, the PVP solution did not obey the Lambert–Beer's law beyond this concentration; therefore, no adsorption experiments were done at higher concentrations for the PVP solution.

The isotherm in Figure 3 also displays the wide, rounded shoulder typical of the broad molecular weight distribution polymer used in the experiments. It also appears from the slope of the isotherm that it is a high affinity type and this high affinity of PVP for adsorption may be considered as due to the high percentage of silica in the clay. This statement is further supported by the observation made by Otsuka et al.[16] who performed adsorption of PVP from an ethanolic solution on different oxides and observed that PVP showed much greater adsorption onto silica then onto alumina. Similarly, in another communication by Ishiduki and Esumi,[5] very low adsorption of PVP was noticed on alumina surfaces. It is well accepted that the greater adsorption of PVP on silica is due to the H-bonding capacity of the oxygen atom (of the pyrrolidone group) with the silanol groups of the silica in hydroxylic solvents.

A negative adsorption was also observed by Esumi et al.[19] while studying the adsorption of PVP on titanium dioxide from an aqueous solution. This was attributed to a greater adsorption of water molecules onto the adsorbent. In our case, however, no such observation was made.

Adsorption Coefficient

Because the adsorption process follows a Langmuir scheme, we can apply the linearized Langmuir equation as given here:

$$\frac{C_e}{a} = \frac{1}{ba_s} + \frac{C_e}{a_s} \tag{2}$$

where a is the adsorbed amount at equilibrium concentration C_e and b and a_s are the adsorption coefficient and adsorption at saturation, respectively.

In accordance with the above equation, a linear plot was drawn between C_e/a and C_e (Fig. 4). From the intercept and slope of the line, the numerical value of b was calculated as 4.17×10^5 mol^{-1}/L. The large numerical value of b indicates that the adsorption process is greatly favored,

and this additionally supports its high affinity nature.

Kinetics of Adsorption

A study of the rate establishment of adsorption equilibrium of polymers at the solid–liquid interface is of fundamental importance in many areas. From a conceptual point of view, the adsorption of polymers implies rate controlling factors that are not encountered with ordinary molecules. In particular because of their chainlike structure, the adsorbed surface films of polymers are structurally similar to the surface of a gel and the rate of adsorption depends not only on the mechanism of adherence to the surface by multiple points of physical adsorption but also on the rate of penetration of gel-like layers. The adsorption rates of polymers were studied in the past.[20] However, the most interesting features were often blurred by trivial ones, for example, mass transfer by diffusion of polymers to the surface, which heavily depends on the hydrodynamic conditions. In some cases it was observed that equilibrium is rapidly established in a few minutes or even a few seconds[21] and, because of experimental difficulties, the kinetic parameter could not be accessed with certainty.

In general, the adsorption of a polymer molecule on a solid surface occurs via a three-step mechanism[22]: transport from the bulk to the surface, attachment to the surface, and rearrangements in the adsorbed layer.

The latter process is often quite slow and in ionic polymers it could be responsible for the claimed irreversibility of the polymers.[23] When we consider the initial stages of the adsorption, only the first and second steps can be considered. When all polymers arriving at the surface immediately adsorb, the adsorption rate is transport limited. This was found in the initial stages of the adsorption of many nonionic polymers.[24] As the adsorption proceeds, the surface becomes increasingly covered with polymer. At a certain point the adsorption is hindered. In this stage the rate of adsorption also depends on the attachment process. At an even higher coverage, the rate becomes independent of the transport process and the attachment is completely rate limiting until the plateau value is reached.

One interesting feature of the polymer adsorption is that the experimental data can be exploited in several ways because numerous kinetic models exist to which the data can be fitted. In the present work, the variation of the amounts of
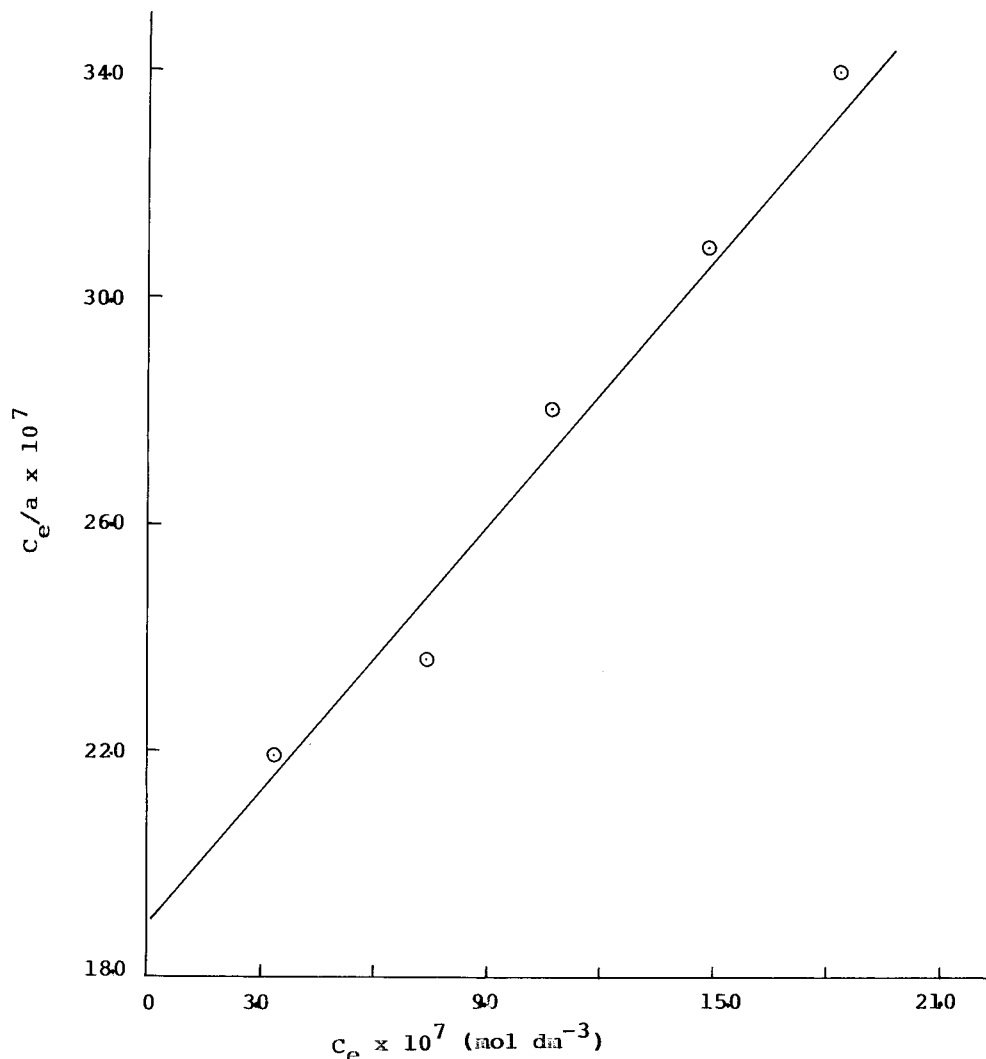
Figure 4   A plot drawn between C_e/a vs C_e for the evaluation of the adsorption coefficient (b).

adsorbed polymer with time is shown in Figure 5. It is clearly implied by the figure that the whole adsorption process can be considered as a two regime process as also postulated for end-functionalized long chains.[25] If we consider the first regime, it is clear that for this short-term kinetics the adsorbed amount of polymer $q(t)$ increases linearly with time, which is indicative of a transported-limited regime where simple Fickian diffusion to the surface is the rate-limiting step. Assuming appropriate boundary conditions (i.e., a well-defined starting point, an initially homogeneous chain concentration in the solution, and a "sink" for adsorption at the surface), the diffusion equation can be solved[26] to yield eq. (3):

$$q(t) = \frac{2C}{\sqrt{\pi}}\sqrt{Dt} \qquad (3)$$

where D is the diffusion constant of the polymer in solution and C is the uniform bulk concentration of the solution. The slope of the curve (Fig. 6) drawn in accordance with eq. (3) gives the diffusion constant as summarized in Table I at the bulk concentration of 16.7×10^{-7} mol/L of the PVP solution.

At later stages, as shown in Figure 6, deviations are observed from the $t^{1/2}$ behavior. This can be assumed to be due to the hindered diffusion of chains through the already adsorbed layer. Ligowe and Leibler[27] considered a simplified model where the adsorbed amount (or the surface coverage) exponentially approaches an equilibrium adsorbed amount q_e with time, introducing a characteristic penetration time T.
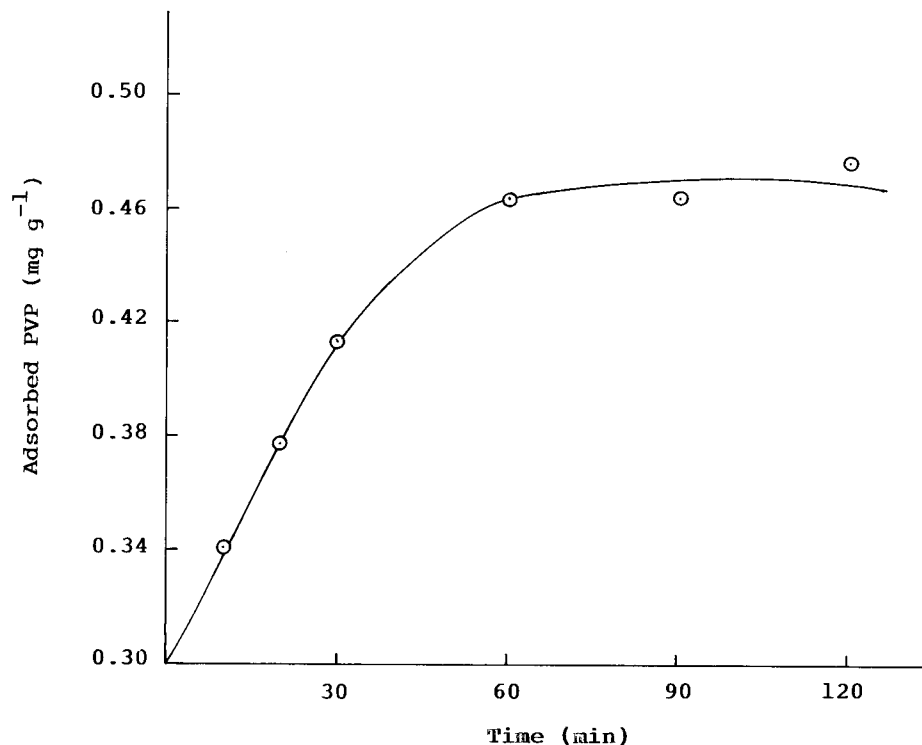
$$q = q_e[1 - \exp(-t/T)] \qquad (4)$$

Figure 5 The variation in the amounts of adsorbed PVP $[q(t)]$ with time t for fixed $[\text{PVP}] = 16.7 \times 10^{-7}$ mol/L, pH 4.2, and $[\text{KNO}_3] = 0.001M$ at $27 \pm 0.2°C$.

Equation (4) indicates that the second process has an exponential nature, and the penetration rate constant $(1/T)$ can be obtained from the slope of $[\ln(q_e - q)]$ as a function of time. The value of the penetration rate constant calculated according to eq. (4) is given in Table I.

Assuming the Langmuirian nature of the adsorption process, the kinetic scheme proposed by Bajpai and Bajpai[28] can be applied, according to which the rate constant for adsorption (k_1) can be evaluated by eq. (5):

$$\frac{1}{C} = k_1 t + \frac{1}{C_0} \qquad (5)$$

where the terms involved have their usual significance. The value of the rate constants for adsorption (k_1) and desorption (k_2) are summarized in Table I.

In a much simplified adsorption rate model by Huguenard et al.[29] the adsorption process was assumed to be of first-order kinetics as

$$N \text{ (solution)} \rightarrow N_s \text{ (interface)} \qquad (6)$$

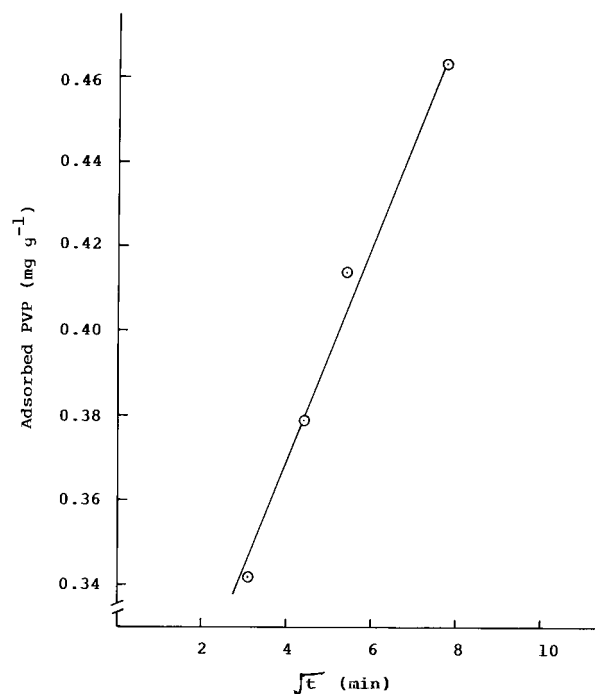$$dN_s/dt \rightarrow N(t) \cdot K(N_s) \qquad (7)$$

Figure 6 A plot drawn between the adsorbed amount $[q(t)]$ and $t^{1/2}$ for the evaluation of the diffusion constant at the same experimental conditions as in Figure 5.

Table I Kinetic Parameters for Adsorption of PVP onto Fuller's Earth

| Initial PVP Concn $C_0 \times 10^7$ (mol/L) | Rate Constant for | | | | Kinetic Coefficient $K(N_s) \times 10^4$ (/min) |
	Adsorption $k_1 \times 10^4$ (/min)	Desorption $k_2 \times 10^9$ (mol/L/min)	Penetration $k_p \times 10^2$ (/min)	Diffusion $D \times 10^8$ (cm²/min)	
16.7	7.26	1.73	4.5	0.0072	6.89

where $N(t)$ represents the instantaneous concentrations of the polymer in the liquid phase and $K(N_s)$ is the kinetic coefficient related to the coverage N_s at time t according to the rate-limiting effect of the available surface. For a given bulk concentration of PVP (16.7×10^{-7} mol/L), the value of $K(N_s)$ (/min) is also presented in Table I.

Effect of pH

The adsorption of polymers onto surfaces is very sensitive to the change in pH of the suspension. The significance of pH in adsorption studies can be understood by the fact that a slight variation in the pH of the suspension not only changes the adsorbed amount but also causes a change in the conformation of the adsorbed polymer, which has a key role in deciding the stability of the suspension. In a broad way the polymer–solid systems can be put into the following three categories:

1. when the polymer and surfaces are both charged (i.e., adsorption of an ionic polymer onto polar oxides);
2. when the polymer and surfaces are both nonionic and there is no effect of pH variation of the system on their charges; and
3. when either of the polymer or surfaces is charged.

There was extensive work on the category 1 type of systems where polyelectrolytes adsorb onto common oxide adsorbents.[30] However, rather few investigations dealt with adsorption of nonionic (or neutral) polymers. The present study falls into category 3 where the polymer (PVP) is totally neutral but the clay surfaces (i.e., Fuller's earth) undergo a charge variation due to some other mechanisms.

In the present case the effect of pH on the adsorbed amounts of PVP was evaluated by varying the pH from 2 to 10 by the appropriate addition of $0.1N$ HCl or NaOH to the suspensions. The results depicted in Figure 7 clearly indicate that

the adsorption isotherm shows a maxima at pH 4.2 and the adsorption decreases at both sides. These types of results are quite often seen in the case of proteins or polyelectrolyte adsorption[31,32] where the maxima of the isotherm is found at the pK_a value or isoelectric point of the protein. The results obtained in the present case are explained below.

To explain the results of the pH effect, we first see how the increasing pH affects the charge on the Fuller's earth surfaces. As mentioned earlier, the basal surfaces of the clay are negatively charged because of the isomorphic substitution of Si^{4+} by Al^{3+} and the charge on this face is considered to be independent of the pH.[33] Nevertheless, the edge charge is positive because of the presence of two different functional groups, each with different dissociation constants and different PZCs, probably from protonation of α—Al_2O_3 and aluminosilicate. The edge charge is positive when the pH < 7 because Al—OH groups undergo protonation and negative when the pH > 7 as mentioned elsewhere.[33]
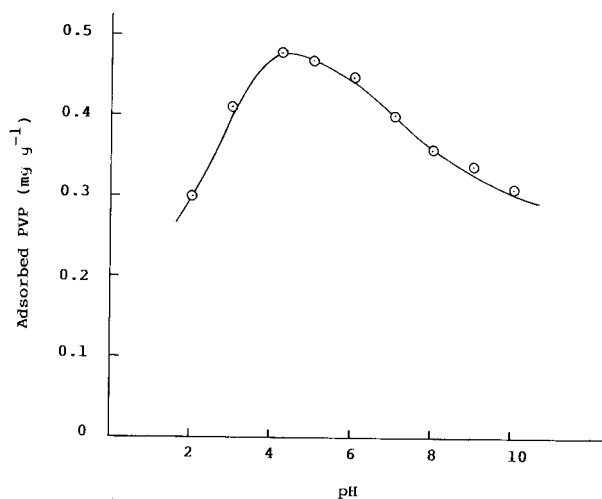

Figure 7 The effect of varying the pH of the PVP–Fuller's earth suspensions on the adsorbed amounts of PVP at fixed [PVP] = 16.7×10^{-7} mol/L and [KNO₃] = $0.001M$ at 27 ± 0.2°C.

When the pH increases above 2 then obviously the PVP molecule does not bear any charge and it has more electronegative oxygen in the pyrrolidone ring and a slight positive charge also. On the other hand, with increasing pH the positive charge on the edge face of the crystal continues to decrease and it gets reversed beyond pH 7. Thus, because of an increase in the negative charge character of the clay surfaces, the H-bond formation between the $AlOH_2^+$ and AlOH and oxygen of the PVP is facilitated and therefore the adsorption continuously increases up to pH 4.2. In fact, this increase should have been continued up to pH 7, which is the PZC of the edge. Presently, we can suppose that there was a shift in the PZC of the clay and this shift occurred toward the acidic range of the pH. Then the shifted PZC was 4.2, which was due to the adsorption of PVP chains on the clay surfaces. It is worth mentioning here that this type of shift is not hypothetical and was also noticed in several adsorption investigations.[34]

Upon further increasing the pH beyond 4.2 at which the maxima of the adsorption isotherm is found, the clay surfaces become totally negatively charged and thus the electrostatic repulsions between the PVP chains and clay surfaces start to increase, which results in a fall in the adsorption. It is important here that beyond pH 4.2, —AlO^- type of groups are formed on the edge face and this obviously makes H-bond formation impossible with the oxygen of the pyrrolidone ring.

Effect of Salts

The presence of ions in a system when a large molecule adsorbs on a solid surface is significant not only because it affects the adsorbed amount but also because it greatly influences the conformation of the adsorbing polymer. In systems where a charged polymer molecule (polyelectrolyte) adsorbs on a charged surface, there are many consequences for the addition of salts[35] to the adsorption system; in such cases the existing electrostatic forces between the polyelectrolyte molecule and surfaces are directly influenced. In fact, there are several electrostatic interactions that may be affected by the ionic strength and specific ionic binding: screening of electrostatic interactions between the polyelectrolyte chains (which would lead to closer packing on the surface and decreased solubility), screening of polyelectrolyte–surface interaction (which would increase adsorption on the negative basal planes), and specific binding of ions to the clay surface or to the polyelectrolyte molecule.
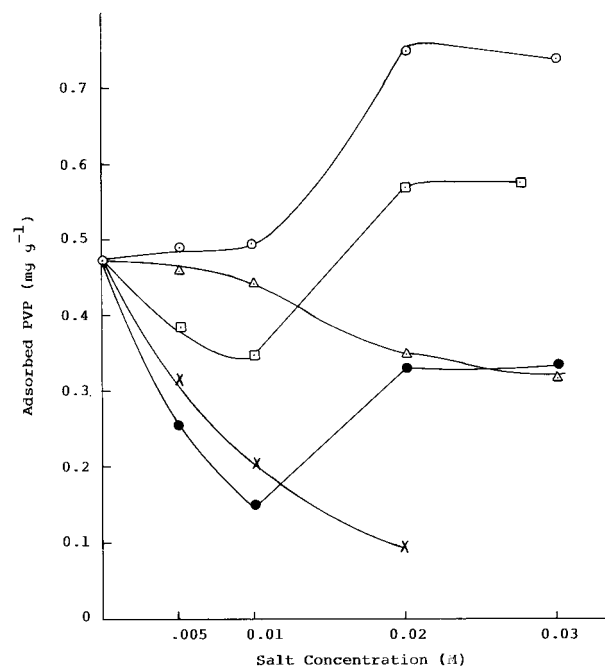

Figure 8 The effect of the addition of anions on the adsorbed amount of PVP at fixed [PVP] = 16.7×10^{-7} mol/L and pH 4.2 at $27 \pm 0.2°C$: (⊙) oxalate, (X) phosphate, (△) chloride, (●) benzoate, and (⊡) propionate.

In the present study, however, the situation is rather different. Because of the nonionic nature of the polymer molecule, the electrostatic interactions (if present) are not affected directly; but in the PVP there is one more important phenomenon that occurs, the "binding of ions" to the PVP molecules, which is a long known property of the polymer and has both fundamental and applied interests.[36] Thus, in the present scenario we studied the effect of the addition of inorganic and organic anions on adsorption. The inorganic ions added were chloride and phosphate (sulfate interfered with the colorimetric estimation of PVP) and the organic anions were benzoate, propionate, and oxalate. The results are shown in Figure 8. They indicate that in the Cl^- and PO_4^{-3} ions the adsorption constantly decreases in the range of 0.005–0.03M and PO_4^{-3} is more effective than Cl^- in causing depression. In the phosphate ion turbidity developed in the supernatent solution beyond a concentration of 0.02M, so no adsorption experiments could be performed beyond that concentration with phosphate ions. In the organic anions the adsorption initially decreases and then starts increasing, attaining almost constant value at higher concentration. In this case the order of effectiveness was benzoate > propionate > oxalate.

⊖ — anions

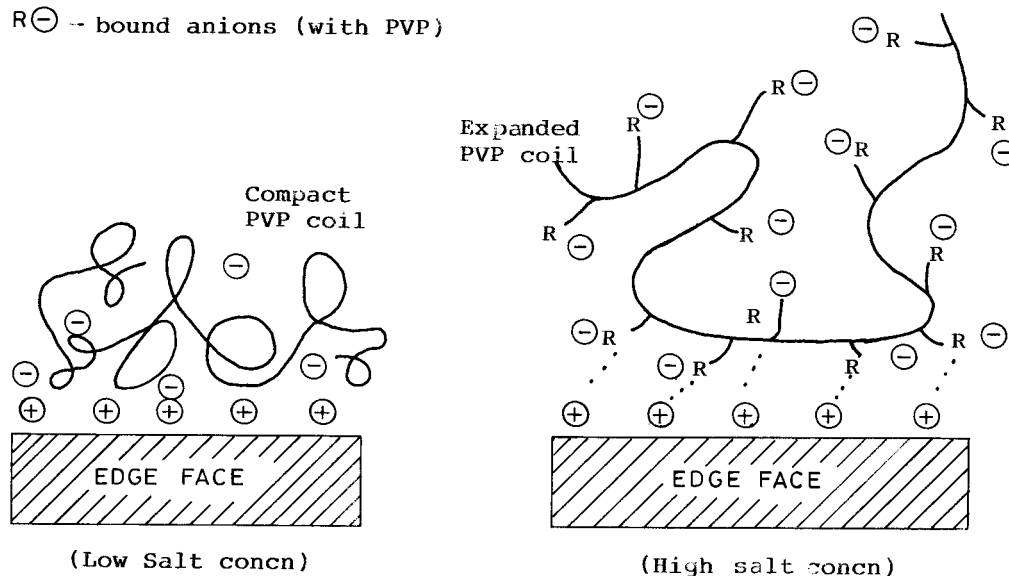R — Pyrrolidone ring

R⊖ — bound anions (with PVP)

Figure 9 A model depicting the adsorption of PVP onto Fuller's earth surfaces at lower and higher salt concentrations.

In the addition of inorganic anions, the added ions may get adsorbed at the positively charged edge face, thus reducing the chance of PVP adsorption on the edge face. This preferential adsorption of anions definitely brings about a fall in the adsorbed amount of PVP. One more possibility is that the added ions screen out the electrostatic attraction between the positively charged edge face and negatively charged oxygen of the pyrrolidone ring, which consequently lowers adsorption. Because phosphate ions are trivalent, they produce a greater effect than chloride ions. Hence, this justifies the observed order of effectiveness.

When organic anions are added to the PVP–Fuller's earth suspension, their impact on adsorption can be explained mainly by the phenomenon of their binding to the PVP coil and the observed contraction–expansion effect produced in the coil.[37] In the lower concentration range (up to $0.01M$) of added anions their binding to the PVP coil does not produce any effect in the expansion of the PVP coil and therefore this does not contribute much to affect the adsorption. At this lower concentration the anions adsorb preferentially to the edge face and cause a depression in the adsorbed amount. However, upon increasing the anion concentration beyond $0.01M$, the

greater complexation of anions with PVP causes polymer coil expansion through long-range Coulombic repulsion between negatively charged molecules bound to the neutral PVP backbone. In this way, the hydrophilic polymer is being converted into a polyelectrolyte. Then because of the expanded conformation of the PVP coil, greater active sites of the coil are exposed to the clay surface and therefore adsorption tends to increase because of the bridging mechanism as modeled in Figure 9. One more aspect for greater adsorption of PVP at higher anion concentration is that, because of the expanded coil, the hydrophobic interaction between the PVP backbone and siloxane layer[38] of the clay becomes operative and this also results in increased adsorption.

The observed order of effectiveness is also justified because the benzoate ion is monovalent while the propionate and oxalate anions are divalent. Thus, the divalent ions are more effective at higher concentration, which is due to their greater charge and size, while the monovalent benzoate ion is predominant at lower concentration.

After a limiting concentration ($0.02M$) of anions, the effects of coil expansion reach their maximum; therefore, beyond this critical salt concen-
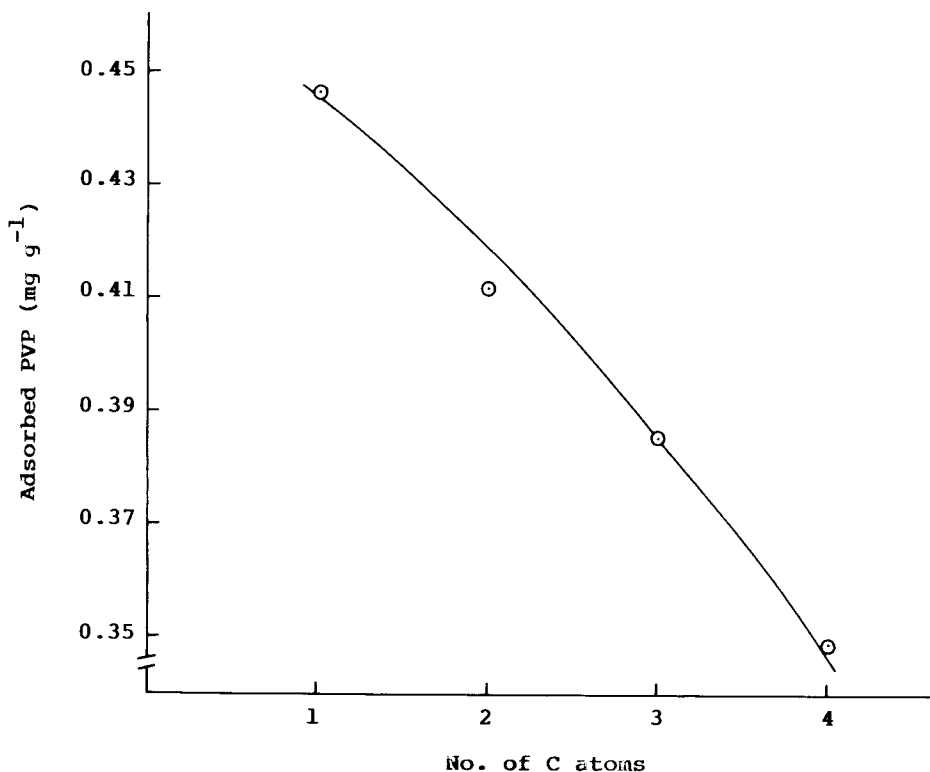
Figure 10 The variation of the adsorbed amount of PVP with the number of carbon atoms of aliphatic alcohols added to the suspensions.

tration $(C > 0.02M)$ the adsorption almost acquires a constant value.

Effect of Solvents

Because PVP has good solubility in other nonaqueous solvents, the role of the solvent becomes much more important because it has a remarkable affect on the shape of the adsorption isotherm. In an adsorption study by Esumi et al.[19] the adsorption of PVP from the binary mixtures of water and alcohols was carried out on different oxides, and they found that increasing the proportion of alcohol in the alcohol–water mixture increased the adsorption of PVP on titanium dioxide. They found that the nature of the medium also affected the conformation of PVP on the surface.

Fuller's earth is well known for its extraordinary adsorptive power toward various organic compounds. Thus, the presence of organic solvents in the PVP–Fuller's earth suspension causes an appreciable change in the adsorption of the polymer. For investigating the role of solvents on adsorption, various aliphatic alcohols were added (10% v/v) to the suspensions, and adsorption was found to constantly decrease with an increasing number of carbon atoms in the alcohol molecule (Fig. 10). The observed order of effectiveness is MeOH < EtOH < n-PrOH < n-BuOH.

The causes of the fall in the adsorbed amounts is because the basal plane of the montmorillonite has a natural tendency to adsorb the organic molecules; and obviously a preferential adsorption of alcohols on the clay surfaces will result in a lower adsorption of PVP; or upon the addition of aliphatic alcohols to the suspensions, the hydrophobic portion of the aliphatic chain of alcohols interacts with the hydrophobic siloxane layer of the clay surface and may be adsorbed. Thus, because of the decrease in number of active sites on the hydrophobic region of the surface, the adsorption of PVP will decrease. Moreover, because the hydrophobic character of added alcohols increases with an increasing number of carbon atoms, the order of effectiveness of added alcohols is also justified.

Effect of Temperature

Because intermolecular forces are often weakened by a rise in temperature, the temperature has a direct influence on the adsorption. In the present work the temperature of the suspension

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was varied between 5 and 40°C, and the results shown in Figure 11 imply that the adsorption decreases with increasing temperature. The following points may be given to explain the results: because of the weakening of binding forces of adsorption with increasing temperature, the adsorption decreases; and at a lower temperature, one cannot rule out the possibility of agglomeration of the PVP molecules, as also suggested in the case of dye adsorption,[39] which will result in an increased adsorption at a lower temperature. As can be seen in Table II, the increased viscosity at lower temperature also supports the idea of agglomeration of the PVP molecules.

The following thermodynamic parameters[40] were also calculated: the standard free energy $\Delta G°$ (kcal/mol), was calculated by using eq. (8).

$$\Delta G° = -RT \ln K \qquad (8)$$

where K is the equilibrium constant of the adsorption process. The value of $\Delta G°$, as calculated above, was found to be -7.66 kcal/mol.

The apparent heat of reaction enthalpy, $\Delta H°$ (kcal/mol), was estimated using eq. (9).

$$\ln\frac{k_1}{k_2} = \frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (9)$$

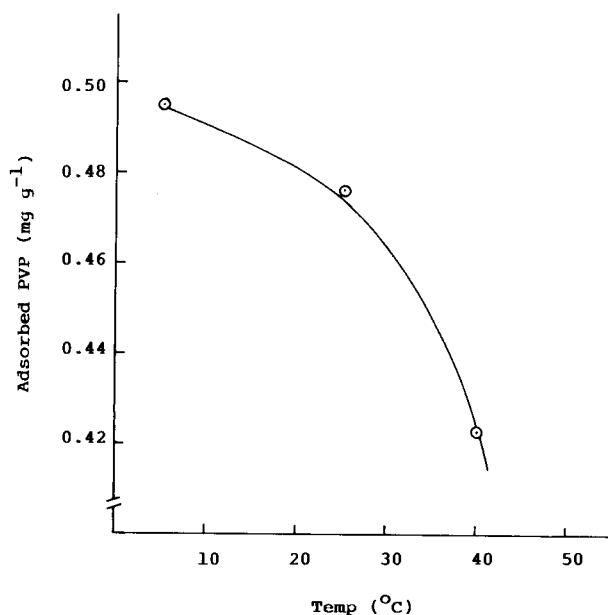The value of $\Delta H°$ was calculated to be -11.8 kcal/mol. Obviously, the negative value of $\Delta H°$

Table II Variation in Viscosity of PVP Solution with Temperature

Temperature (°C)	η_{rel}
5	1.44
35	1.23

indicates the exothermic nature of the adsorption process.

The entropy, $\Delta S°$ (cal/deg mol), of the system was calculated using eq. (10).

$$\Delta G° = \Delta H° - T\Delta S° \qquad (10)$$

The value of $\Delta S°$ was found to be -14 cal/deg mol.

CONCLUSIONS

Adsorption of PVP onto Fuller's earth surfaces in aqueous suspensions mainly occur via H bonding of the oxygen of the pyrrolidone ring and positively charged aluminols of the edge face of the montmorillonite crystal that is a major constituent of the Fuller's earth. The adsorption is Langmuirian in nature and exhibits two regime kinetic curves. The adsorbed amount is sensitive to the pH change and shows the maxima at a particular pH, which is identified as the "shifted zero point charge" of the aluminols of the edge face. The adsorption also decreases when chloride and phosphate anions are added to the suspensions. With the organic anions the adsorption initially decreases and then increases beyond a critical concentration ($0.01M$). The temperature and organic solvents have inverse effects on the adsorbed amount.

REFERENCES

1. Fleer, G. J.; Scheutjens, J. M. H. M. In Coagulation and Flocculation; Dobias, B., Ed.; Marcel Dekker: New York, 1993.
2. Tadros, Th. F., Ed. Solid/Liquid Dispersions; Academic: New York, 1987.
3. Molyneux, P. In Water-Soluble Synthetic Polymers: Properties and Behavior; CRC Press: Boca Raton, FL, 1987; Chap. 2.
4. Popping, B.; Deratani, A.; Sebille, B.; Desbois, N.; Lamarche, J. M.; Foissy, A. Colloids Surfaces 1992, 64, 125.
5. Ishiduki, K.; Esumi, K. Langmuir 1997, 13, 1587.
6. Bajpai, A. K. Prog Polym Sci 1997, 22, 523.

Figure 11 The effect of the temperature of the adsorption medium on the adsorbed amount of PVP.

7. Clark, A. Q.; Herrington, T. M.; Petzold, J. C. Colloids Surfaces 1990, 44, 247.

8. Parnas, R. S.; Chaimberg, M.; Taepaisitphongse, V.; Cohen, Y. J Colloid Interface Sci 1989, 129, 441.

9. Smith, J. A.; Galan, A. J Colloid Interface Sci 1995, 29, 685.

10. Brandrup, J.; Immergut, E. H., Eds. Polymer Handbook; Wiley–Interscience: New York, 1967.

11. Bajpai, A. K.; Rajpoot, M. Bull Chem Soc Jpn 1996, 69, 521.

12. Bajpai, A. K.; Dengre, R. Ind J Chem Technol 1997, 4, 113.

13. Snell, F. D.; Snell, C. T. In Colorimetric Methods of Analysis; Van Nostrand: Princeton, NJ, 1961; p 189.

14. Bell, Funsten. Industrial Rocks and Minerals; American Institute of Mining and Metallurgical Engineers: New York, 1937; Chap. VII.

15. Maltech, P. C.; Somasundaran, P.; Kulkarni, R. A.; Gundiah, S. Langmuir 1991, 7, 2108.

16. Otsuka, H.; Esumi, K.; Ring, T. A.; Li, J. Th.; Caldwell, K. D. Colloids Surfaces 1996, 116, 161.

17. Giles, C. H.; Macewan, T. H.; Nakhwa, S. N.; Smith, D. Chem Soc Faraday Trans 1963, 4, 3973.

18. Cohen Stuart, M. A.; Fleer, G. H.; Bijsterbosch, B. H. J Colloid Interface Sci 1982, 90, 310.

19. Esumi, K.; Ishiduki, K.; Otsuka, H.; Ono, M.; Kchikawa, S.; Yanase, C. J Colloid Interface Sci 1996, 178, 549.

20. Lipatov, Y.; Sergeeva, L. M. In Adsorption of Polymers; Wiley: New York, 1974.

21. Stromberg, R. R.; Kline, G. M. Mod Plast 1961, 4, 20.

22. Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J. J Colloid Interface Sci 1996, 182, 133.

23. Meadows, J.; Williams, P. A.; Garvey, M. J.; Harrop, R. A.; Phillips, G. O. Colloids Surfaces 1988, 32, 275.

24. Dijit, J. C.; Cohen Stuart, M. A.; Hofman, J. E.; Fleer, G. J. Colloids Surfaces 1990, 51, 141.

25. Pankewitsch, T.; Vanhoorne, P.; Jerome, R.; Stamm, M. Macromolecules 1995, 28, 6986.

26. Motschmann, H.; Stamm, M.; Toprakcioglu, C. Macromolecules 1991, 24, 3681.

27. Ligowe, C.; Leibler, L. J Phys 1990, 51, 1313.

28. Bajpai, U. D. N.; Bajpai, A. K. Polym Int 1993, 32, 43.

29. Huguenard, C.; Varoqui, R.; Pefferkorn, E. Macromolecules 1991, 24, 2226.

30. Tanaka, H.; Odberg, L.; Wagberg, L.; Lindstrom, T. J Colloid Interface Sci 1990, 134, 219.

31. Leprince, F.; Quiquampoix, H. Eur J Soil Sci 1996, 47, 511.

32. Bajpai, A. K.; Bajpai, S. K. Colloid Polym Sci 1995, 273, 1023.

33. Flegmann, A. W.; Grodwin, J. W.; Ottewill, R. H. Proc Br Ceram Soc 1969, 13, 31.

34. Douzou, P.; Petsko, G. A. Adv Protein Chem 1984, 36, 245.

35. Blaakmeer, J.; Bohmer, M. R.; Cohen Stuart, M. A.; Fleer, G. J. Macromolecules 1990, 23, 2301.

36. Molyneux, P. Asian Pacif J Allerg Immunol 1984, 2, 301.

37. Klech, C. M.; Cato, A. E.; Sattle, A. B. Colloid Polym Sci 1991, 269, 643.

38. Jaynes, W. F.; Boyd, S. A. Clays Clay Miner 1991, 39, 428.

39. Giles, C. H.; Eston, I. A.; Mekay, R. B. J Chem Soc 1964, 4, 4495.

40. Doula, M.; Ioan, A. N.; Dimirkou, A. Commun Soil Sci Plant Anal 1995, 26, 1535.