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ORIGINAL CONTRIBUTION

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Dynamic measurements of adsorption of hydrolyzed polyacrylamide (HPAM) onto hematite

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Abstract The adsorption measurements of hydrolyzed polyacrylamide (HPAM) onto hematite suspension are carried out to study the dynamics of the polymer adsorption onto the suspension particles and to investigate the mode of the polymer adsorption. The polymer is found to show much affinity for the adsorption because of the opposite charges possessed by the polymeric flocculant and the suspension particles. Various adsorption parameters such as adsorption coefficient, the rate constants for the adsorption and desorption, are evaluated with the help of a recently proposed kinetic scheme. It is found that the extent of adsorption and the adsorption rate are adequately affected by increasing the pH of the suspension while, unexpectedly, the adsorption is found to show only a marginal increase on addition of Na_2SO_4. Both the amount of the adsorbed polymer and the adsorption rate are also found to increase with the degree of hydrolysis of the polyelectrolyte.

Key words Hydrolyzed polyacrylamide – hematite – adsorption – kinetics

Introduction

The adsorption behaviour of polymers onto inorganic particles is of great practical importance. For instance, physical benefaction of mineral slimes by selective flocculation is one of the promising fields in the area of fine particle technology and is totally based on the phenomenon of adsorption. Though the adsorption of both uncharged and charged polymers onto planar and particulate surfaces has been extensively investigated [1–4], the majority of the studies were mainly focused to examine the static aspects of the adsorption and rather little attention was paid on the kinetic behaviour of the adsorption process.

The present paper aims at studying the dynamics of the adsorption of hydrolyzed polyacrylamide (HPAM) onto the iron oxide particles with an extremely simple rate expression model [5–7] which enables one to evaluate the parameters like adsorption coefficient and rate constants for adsorption and desorption.

Experimental

Materials

Polyacrylamides (PAM) of varying molecular weights were synthesized by polymerizing acrylamide using Ce^{4+}/sodium sulphite redox pair at room temperature [8]. The PAM samples so obtained were hydrolyzed [9] to give copolymers of polyacrylamide and polyacrylic acid of varying compositions. The degree of hydrolysis was determined by the method of potentiometric titration [10]. The characteristics of the HPAM samples used in the study are listed in Table 1.

Table 1 Characteristics of polymer samples (HPAM) used in the study

Polymer sample	Mol. Wt. $\times 10^{-4}$ (Viscosity average)	% Hydrolysis
Hydrolyzed Polyacrylamide (HPAM-1)	5.0	22.0
(HPAM-2)	4.2	36.8
(HPAM-3)	3.7	48.0
(HPAM-4)	3.0	62.6
(HPAM-5)	2.5	70.8

Adsorbent

The hematite powder (α-Fe_2O_3) was supplied by the BDH (Pule, England). The specific surface area of the powder measured by the BET method using N_2 as an adsorbate was 14.2 $m^2 g^{-1}$. The zero point charge (zpc) of the oxide was found to be 6.8 as determined by the usual titration procedure.

Method

The method for carrying out the adsorption experiment involves shaking a known volume of HPAM solution of definite concentration in a pyrex beaker containing a fixed amount of preconditioned hematite powder (0.4 g) at pH 4.0 and ionic strength at 0.01 $MKNO_3$. The quantity of adsorbed HPAM was determined by the method of Scoggins and Miller [11]. In brief, the method of analysis consists of reacting bromine (at pH 3.5) with partially hydrolyzed polyacrylamide solution to give a product that oxidises iodide ion to iodine. The iodine liberated is measured spectrophotometrically as the starch-tri-iodide complex. The strength of the complex is proportional to the concentration of polyacrylamide in solution. The details about the effect of metal ions, reaction time, pH of the solution etc. on the final estimation of polymer content are described elsewhere [11].

For kinetic measurements definite aliquots of the agitating suspension were withdrawn at definite time intervals and the remaining HPAM after adsorption was estimated as referenced above.

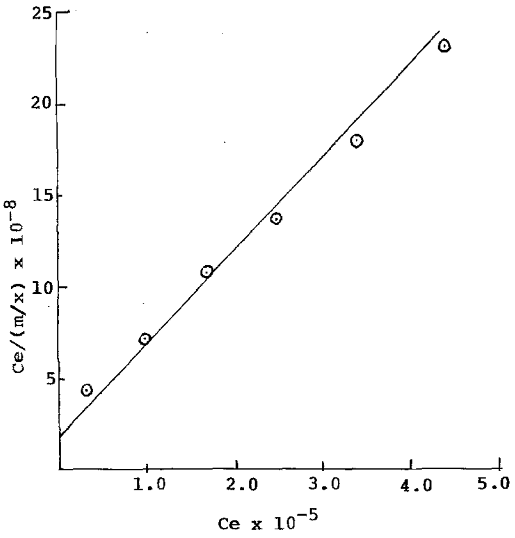

Fig. 1 Plot of $C_e/(m/x)$ vs. equilibrium concentration (C_e) for the adsorption of HPAM (22%) onto hematite at pH 4.0 and ionic strength at 0.01 $MKNO_3$

Adsorption coefficient (k_1/k_2)

For the evaluation of adsorption coefficient ($= k_1/k_2$) a plot is drawn between $Ce/(m/x)$ and Ce values which yields a straight line in accordance with the following Langmuir equation,

$$\frac{Ce}{(m/x)} = \frac{Ce}{k} + \left(\frac{k_1}{k_2}\right) \cdot \frac{1}{k},$$

where k' is a constant. The straight line so drawn is shown in Fig. 1 and the numerical value of the adsorption coefficient as calculated from the slope and intercept has been found to be 2.33×10^5 l mol^{-1}.

Evaluation of the rate constants

The numerical values of the rate constants for adsorption (k_1) and desorption, (k_2) are calculated by the Eq. (10) of reference [6] according to which

$$\frac{1}{C} = \frac{k_1}{C_0} t + \frac{1}{C_0},$$

where C_0 = initial concentration of polymer solution; C = remaining concentration of polymer solution at time t.

As the equation implies that a plot drawn between $1/c$ and t would be a straight line and from the slope of which the value of k_1 may be calculated. In Fig. 2 this plot has been drawn and the value of k_1 is found to be $1.71 \times 10^{-4} s^{-1}$. Now when both the values k_1/k_2 and k_1 are known, the value of k_2 may easily be calculated as found to be 1.37×10^{-8} mol $l^{-1} s^{-1}$.

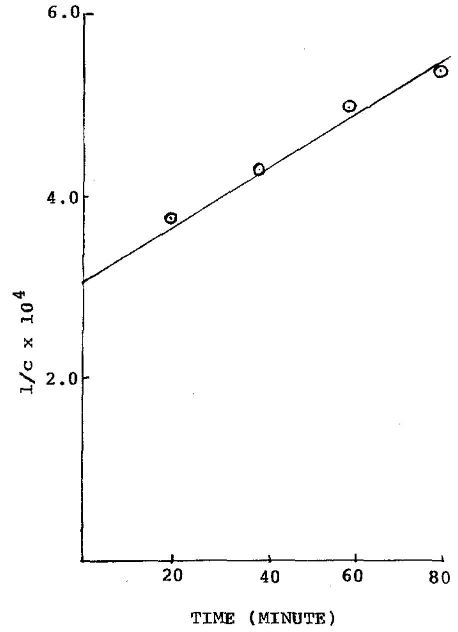

Fig. 2 Plot of $1/c$ vs. time t for the adsorption of HPAM (22%) onto hematite at pH 4.0 and ionic strength at 0.01 M KNO_3

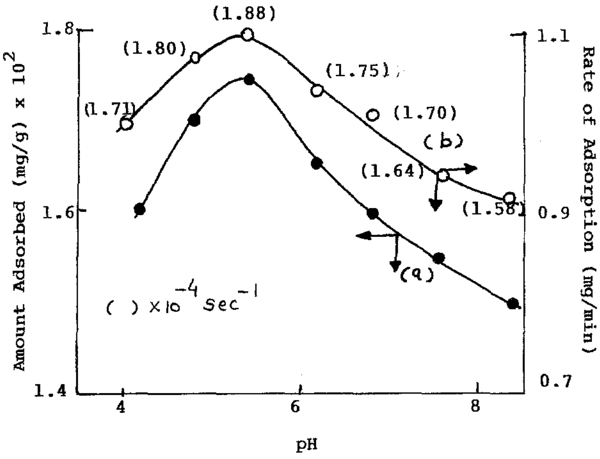

Fig. 3 Effect of varying pH of HPAM solution (22%) on its a) Plateau adsorption, and b) the initial rate of adsorption (R_{ad}) onto hematite at fixed ionic strength at 0.01 M KNO_3. The data in parentheses show the rate constants at respective pH

Factors affecting adsorption

pH Effect

The pH of a solution is one of the most important parameters that significantly affects the rate of any physical or chemical process. Its role becomes undoubtedly much more prominent when the reaction medium involves various ionic species.

In the present study for investigating the role of pH in the adsorption of HPAM, the pH of the medium was varied from 4 to 8.4 by adding 0.15 M NaOH to the polymer solution at the ionic strength of 0.01 M KNO_3. It is clear from Fig. 3(a) that initially the plateau adsorption increases and after pH 5.4 it starts decreasing. The initial increase observed is quite uncommon and may be explained by the fact the with increase in pH of the medium, the weak polyelectrolyte (HPAM) undergoes ionization and consequently the newly generated COO^- groups get adsorbed on the oppositely charged surface bringing about an increase in the adsorbed mass. But after a definite pH (5.4 in the present case) the number of COO^- groups becomes so large in number that an electrostatic repulsion begins to act along the macromolecular coil. Obviously, this repulsion causes an increase in the dimension of the polymer molecule and, therefore, the adsorption decreases.

One more factor that also accounts for the observed fall in the adsorption is that on increasing the pH of the solution beyond 5.4, the hematite particles acquire a negative charge and due to the electrostatic repulsion between the surface and the polyelectrolyte molecules the adsorbed mass decreases. Here it is important to see that the experimentally determined zero point charge (ZPC) of the hematite is 6.8 and, therefore, one must expect the surface to become negatively charged beyond 6.8 only. But in the present case the negative charge is developed beyond 5.4 which may be attributed to the fact the a shift of ZPC to the lower side is observed when the amide groups of PAM are adequately hydrolyzed (22%) [12]. A similar type of observation has also been noticed by other workers [13].

The quantitative effect of pH on the dynamics of the adsorption has also been studied. For this purpose adsorption experiments were carried out at respective pH and the adsorbed mass vs. time curves for each run were obtained. The slopes of the initial portion of the curves (not included in the text) were calculated and plotted as the initial rate of adsorption (R_{ad}) against the pH of the solution as shown in Fig. 3(b). It is evident from the figure that the variation of rate of adsorption with pH is almost similar to that of the adsorbed mass at saturation. The initial rise in R_{ad} followed by a fall beyond the pH 5.4 may be explained as follows:

As is well known, the rate of adsorption depends on i) the transport of the mass towards interface and ii) the attachment of polymer molecules to the surface. It is worth mentioning here that whereas the first step of the adsorption dynamics clearly indicates the diffusibility of the polymer molecules from the bulk to the surface, on the other hand, the second step is only concerned with the fact of how many polymer molecules get attached to the active sites of the surface in unit time. To test if the rate of adsorption (R_{ad}) could be controlled by the first step, we performed the kinetic runs at varying speeds of agitation and found that the rate of adsorption was almost unaffected by the speed. This observation clearly precludes the dependence of R_{ad} on the first step. Hence, clearly, it should be the attachment of molecules that decides the rate of adsorption. Now at a given time interval the number of molecules reaching interface is almost the same for all pH values, but there is a difference in their rates of attachment to the surface. As the pH rises the number of COO^- groups in HPAM molecules increases and, as a consequence, the polyelectrolyte molecules become increasing negatively charged. Obviously a strong and favorable electrostatic interaction will result in an enhanced rate of adsorption. In fact, below pH 5.4 there are acting two types of driving forces for adsorption viz., electrostatic attraction and H-bonding. Below the ZPC of the surface both the forces tend to favour the adsorption but at higher pH (> ZPC) when the surface acquires a negative charge the electrostatic repulsion opposes the adsorption while H-bonding favours it. Therefore, the number of molecules attached to the surface starts decreasing, which consequently results in a lower rate of adsorption. The rate constants for the adsorption have also been calculated at different pH and given in Fig. 3(b).

Salt effect

The role of low molecular weight compounds in the adsorption studies of polyelectrolytes is of prime interest as their presence in the solution affects the process of adsorption in many ways.

In the present study the effect of addition of salts on the adsorption behaviour of HPAM has been studied by adding varying concentration of Na_2SO_4 to the adsorption medium. It is clear from Fig. 4(a) that when the concentration of added salt varies between 0.02 to 0.12 M, a marginal increase in plateau adsorption is observed. The result observed is not in complete agreement with those reported by the majority of workers [14, 15] in which a remarkable increase in the adsorption has been noticed. The reason for such a feeble dependence of plateau adsorption on salt concentration may be attributed to the fact that at experimental pH (4.0) the hematite particles had a net positive charge and, therefore, the possibility of the adsorption of SO_4^{2-} ions on the particles surfaces may not be ruled out.

Another reason that also explains the small influence of ionic strength is that the added SO_4^{2-} ions screen the positive charge of the surface which consequently results in a weaker electrostatic attraction between the polymer molecules and the hematite particles. Also, at the experimental pH 4.0 the polymer molecules are not much ionized. Both these factors result in a small increase in the adsorbed polymer.

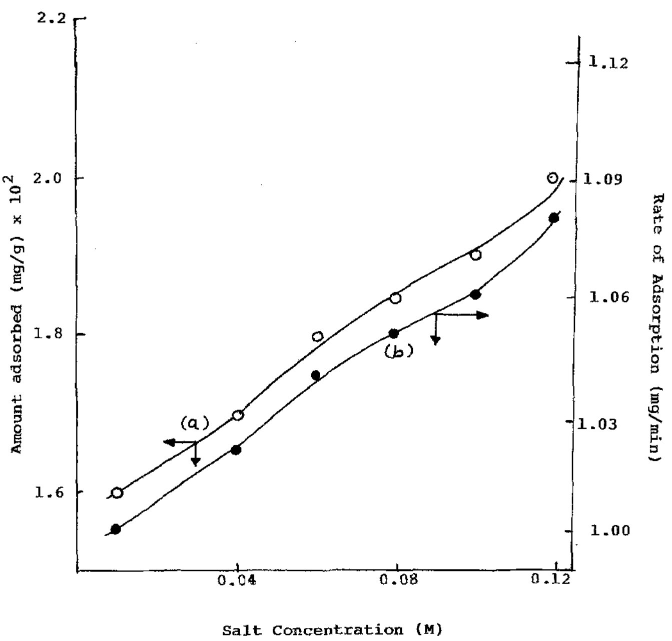

Fig. 4 Effect of addition of Na_2SO_4 on a) Plateau adsorption, and b) the initial rate of adsorption (R_{ad}) of HPAM (22%) onto hematite at fixed pH 4.0

The effect of the added salt concentrations on the initial rate of adsorption is shown in Fig. 4(b). The figure clearly indicates that there is only a marginal increase in the initial rate of adsorption with increasing ionic strength of the medium. The reason for this behaviour is quite obvious as an increase in the ionic strength of the medium does not appreciably increase the extent of attachment of the polymer molecules to the surface as explained in the last two paragraphs. Since the ionic strength hardly affects the adsorption rate, the rate constants for the adsorption have not been evaluated.

Effect of degree of hydrolysis

For studying the effect of degree of hydrolysis five samples of HPAM with different degrees of hydrolysis were used at a constant pH of 4.0 and ionic strength at 0.01 M KNO_3. It is clear from Fig. 5(a) that the plateau adsorption gradually increases when HPAM fractions with increasing degree of hydrolysis are used. The increase observed may be explained as below:

With increasing degree of hydrolysis of the polymer the number of COOH groups in HPAM molecules increase and a few of them get ionized to give COO^- ions, thus imparting a negative charge to the polymer molecules.

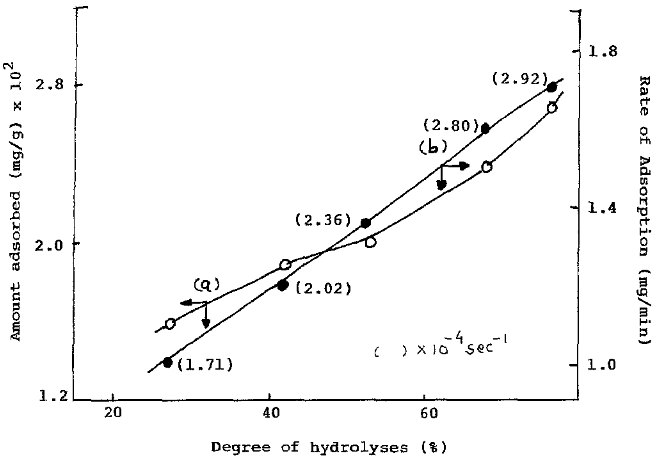

Fig. 5 Effect of degree of hydrolysis of HPAM on its a) Plateau adsorption, and b) the initial rate of adsorption (R_{ad}) onto hematite at fixed pH 4.0 and ionic strength at 0.01 M KNO_3. The data in parentheses shows the rate constants for respective degree of hydrolysis of HPAM

Obviously, a greater degree of hydrolysis implies a greater extent of negative charge on the HPAM molecules. Now, since the experiment is being carried out at pH 4.0 (< ZPC), the surface acquires a positive charge and, consequently, an electrostatic attraction between the polymer molecules and surface of the hematite particles begins to act which results in an increased adsorption. Similar results have also been reported by other workers [16]. One more factor that may account for the observed increase is that with increasing COOH groups on the polymer molecule the intramolecular H-bonding between the acid and the amide groups increases, which shortens the macromolecular coil and, consequently, the adsorption increases. However, we have not observed any remarkable change in viscosity of HPAM solutions with change in the degree of hydrolysis.

The effect of the degree of hydrolysis on the initial rate of adsorption has also been studied and shown in Fig. 5(b) which clearly implies that the rate of adsorption increases when the degree of hydrolysis of HPAM molecules varies between 22 to 70.8%. The rate constants for the adsorption of HPAM samples of varying degree of hydrolysis have also been calculated and given in Fig. 5(b).

Conclusions

The adsorption of HPAM onto hematite suspension is studied at pH 4.0 when the surface is positively charged. The adsorption is found to increase with the rising pH but decreases after a definite pH value. The adsorption is surprisingly not much affected by the addition of Na_2SO_4 to the medium which is justified on the basis of competing adsorption onto hematite particles by both the salt anions and polyions. It is also observed that the degree of hydrolysis of the polymer greatly affects the extent of adsorption. A change in experimental conditions like the pH, ionic strength and degree of hydrolysis also affects the initial rate of adsorption and therefore the adsorption rate constants.

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