Kinetics of flocculation of iron oxide particles by polyacrylamide

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The kinetics of the flocculation of iron oxide sol by polyacrylamide has been studied by turbidity measurements. Various kinetics parameters such as per cent flocculation, flocculation rate and rate constants for the flocculation and deflocculation have been evaluated. Both the qualitative and quantitative effects of various parameters such as polymer dosage, pH of the suspension, salt concentration and molecular weight of the polymeric flocculant on the kinetics of flocculation have also been investigated.

In a boiling test-tube (pyrex) a definite volume of hematite sol was taken at a constant pH (4.0) and required ionic strength (1 x 10⁻⁴ mol dm⁻³), and potassium nitrate (KNO₃) was added to it. A fixed volume of polyacrylamide solution of definite concentration was added to this suspension. After mixing the solutions, the test-tube was shaken for 30 min gently. The mixture was then mildly centrifuged for 2 min and the turbidity (in NTU) of the supernatant solution was measured with a turbidity-meter (NT Meter 131, Systronics, India).

For following the kinetic course of flocculations several identical test-tubes containing mixtures of polymer and suspension of the same compositions were shaken simultaneously and at different time intervals test-tubes were taken out of the shaker, centrifuged and turbidity of the respective supernatants was recorded.

Flocculation and deflocculation constants—For evaluating the flocculation and deflocculation rate constants, the following equations were used as described by Heimenz and Vold¹⁰.

\[ T_s = \frac{\beta}{k} \]  \hspace{1cm} ... (1)

and

\[ \ln \frac{T - T_s}{T_s - T_o} = \beta t \]  \hspace{1cm} ... (2)

where, \( T_s \) is the specific rate constant for flocculation, \( \beta \) is the specific rate constant for deflocculation, \( T \) is the turbidity of supernatant at time \( t \), \( T_s \) is the initial turbidity of iron oxide sol, \( T_o \) is the turbidity at steady state (or equilibrium).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \bar{M} \times 10^{-4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM-I</td>
<td>5.0</td>
</tr>
<tr>
<td>PAM-II</td>
<td>4.2</td>
</tr>
<tr>
<td>PAM-III</td>
<td>3.7</td>
</tr>
<tr>
<td>PAM-IV</td>
<td>3.0</td>
</tr>
</tbody>
</table>
The extent of flocculation has been calculated in terms of the % flocculation as given below,

\[
\% \text{ Flocculation} = \left( \frac{T_0 - T}{T_0} \right) \times 100 \quad \ldots (3)
\]

### Results and Discussion

**Role of electrolyte**—It has been well established from a number of investigations\(^1\)\(^2\) that the presence of an electrolyte is essentially required to induce flocculation. In the present work, the effect of concentration of KNO\(_3\) (0.6-1.0 \times 10^{-4} \text{ mol dm}^{-3}) on the turbidity of the iron oxide sol, after a duration of 30 min, has been studied. As shown in Fig. 1, no flocculation occurs without KNO\(_3\), and as expected KNO\(_3\) also could not flocculate the suspension when added alone. At each of the KNO\(_3\) concentrations, an optimal flocculant concentration was observed at which minimum turbidity is obtained. This optimum value decreased with the increase in KNO\(_3\) concentration as 40.0, 25.0 and 17.0 mg g\(^{-1}\) at 0.6, 0.8 and 1.0 \times 10^{-4} \text{ mol dm}^{-3}, respectively. Above this optimum value the turbidity increased due to restabilization of the sol. Similar type of observations have also been reported by other workers\(^12\).

**Effect of polymer dosage**—The effect of concentration of the flocculant has been investigated by adding polyacrylamide in the range 16.0-83.5 mg g\(^{-1}\) of iron oxide. For this purpose increasing amounts of PAM were added to the iron oxide sol and turbidity of the suspension was recorded after shaking for 30 min. The results obtained are shown in Fig. 2 which clearly reveal that the percent flocculation increases with the increase in polymer dosage and there is an optimum dosage of the polymer at which the maximum percent flocculation is observed. The value of optimum polymer dosage has been predicted\(^13\)\(^14\) as that dose of polymer at which the surface coverage of the solid by adsorbed polymer is half. Since the adsorption of polymer onto iron oxide particles is one of the fundamental causes of flocculation, the adsorption of PAM onto iron oxide particles has also been studied\(^15\) and it was found that the plateau value starts at 33.0 mg g\(^{-1}\) of PAM at 1 \times 10^{-4} \text{ mol dm}^{-3} of KNO\(_3\). Assuming a surface coverage of unity at the plateau value, the optimum dosage has been predicted as 16.5 mg g\(^{-1}\) of PAM which is much nearer to the observed experimental value of 17.0 mg g\(^{-1}\) of PAM. Beyond the optimum dosage, the polymer tends to restabilize the suspension which is indicated by the increased turbidity of the supernatant after maximum flocculation. The restabilization of the suspension is commonly attributed to the fact that beyond the optimum dosage, the polymer builds up a protective sheath around individual particles, thereby stabilizing the dispersion due to steric repulsion.

**Kinetics of flocculation**—In order to follow the kinetic course of the flocculation process the turbidity of the supernatants has been monitored at
different time intervals as shown in Fig. 3. It is clear from this figure that the rate of turbidity change is almost constant up to 20 min and, therefore, the rate constants for flocculation and deflocculation may easily be calculated by using Eqs (1) and (2) respectively. The results clearly imply that the extent of flocculation increases with time as shown by the decrease in turbidity of the supernatants at different time intervals for respective polymer dosage. The results obtained are in accordance with the adsorption experiments where the rate of adsorption was found to increase with the increase in polymer concentration. Obviously increased adsorption of PAM onto iron oxide particles tends to flocculate the suspension with greater rate.

The rate constants for flocculation and deflocculation, and flocculation rate have also been calculated and the values obtained are summarized in Table 2. The data obtained evidently support these facts.

**Effect of pH**—In flocculation investigations, the pH of the suspension plays a significant role in affecting the flocculation characteristics of the polymer-suspension system. It has been noticed that a slight variation in the pH of the system brings about a large change in the charge profile of both the flocculant and the suspension. This obviously results in a change in the electrostatic forces of attraction on which the process of flocculation is fundamentally dependent.

In the present investigation, the pH of the iron oxide suspension has been varied from 1.5 to 8.5 and effect on per cent flocculation and the rate constants for flocculation and deflocculation have been studied. As shown in Fig. 4, the per cent flocculation constantly decreases with increase in the pH of suspended medium. It is also expected that with decrease in per cent flocculation the rate of flocculation should also fall which has been calculated and summarized in Table 3. The reason for the observed decrease may be outlined as follows:

(i) In the acidic pH range of 1.0-5.0, both the
floculant and suspended particles are positively charged. The larger per cent flocculation of the suspension may be explained due to the greater adsorption of PAM molecules on the iron oxide particles via the H-bond formation between the polar C = O group and positively charged hematite surface\textsuperscript{16,17}. As the pH of the solution increases the positive charge over the iron oxide particles decreases which results in a weakening of the electrostatic attractive forces and, hence the decrease in flocculation.

(ii) In the alkaline range, the iron oxide acquires a negative charge due to FeO\textsuperscript{-} type of groups\textsuperscript{18} on the surface and, therefore, one has to preclude the possibility of H-bond formation due to electrostatic repulsion between the polar C = O groups and the particle surfaces.

Effect of salt—The effect of ionic compounds having low molecular weight, on the extent of flocculation has been investigated by adding different anions of sodium in the concentration range 0.10-0.40 \times 10^{-3} \text{ mol dm}^{-3}. The results obtained for the addition of NaCl, Na\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{3}PO\textsubscript{4} have been shown in Fig. 5. The most salient feature is that the extent of flocculation increases from nearly zero to completion, over a relatively narrow range of salt concentration (C\textsubscript{sal}C\textsubscript{sc}). Apparently, a certain critical concentration of salt is needed to ensure flocculation. It is also revealed from Fig. 5 that the per cent flocculation increases with the increasing salt concentration and the effectiveness of the added salts increase in the following order:

\text{Cl}^{-} < \text{SO}_{4}^{2-} < \text{PO}_{4}^{3-}

![Fig. 5—Effect of varying concentrations on the % flocculation of iron oxide sol at fixed pH 4.0](image)

Molecular weight effect—The molecular weight of a polymeric floculant plays a key role in deciding its effectiveness towards flocculation. This is due to the fact that the molecular weight not only changes the amount of the adsorbed polymer but also provides some information about the conformation of the adsorbed polymer.

In the present investigation, the effect of the molecular weight of PAM on the extent and rate of flocculation has been studied by taking polyacrylamide of varying molecular weights at the same pH and ionic strength of the medium. The results obtained are shown in Fig. 6 which clearly indicates that percent flocculation increases with the increasing molecular weight. The observed increase may be attributed to the fact that the polymer molecule with higher molecular weight will adsorb onto greater number of particles thus bridging them together to produce flocculation.

The influence of molecular weight on the kinetics of flocculation was observed and found that the flocculation rate increases with increase in the molecular weight of the floculant. The results have been summarized in Table 4, which clearly imply that the rate constants for flocculation increase with increasing molecular weight. The
causes for the observed increase is quite obvious because a flocculant molecule with larger molecular weight will contain greater number of active sites and consequently large number of iron oxide particles will be flocculated.

Table 4—Effect of varying molecular weight of PAM on the kinetic parameters of flocculation of iron oxide sol, at a fixed pH 4.0 and ionic strength of 1.0 × 10^{-1} M KNO₃

<table>
<thead>
<tr>
<th>Molecular weight (× 10^{-1})</th>
<th>Flocculation rate constant (A) × 10^{9}, s^{-1}</th>
<th>Deflocculation rate constant (B) × 10^{9}, s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>3.7</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>4.2</td>
<td>5.6</td>
<td>4.5</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Fig. 6—Variation in % flocculation of the iron oxide sol with varying molecular weights of PAM at fixed pH 4.0 and at ionic strength of 1.0 × 10^{-1} M KNO₃.