Adsorption Kinetics of Polyamide-epichlorohydrin on Cellulosic Fibres Suspended in Aqueous Solution

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Abstract: The adsorption kinetics of polyamide-epichlorohydrin wet-strength resin in aqueous papermaking fibrous suspension was investigated using colloid titration and adsorption modeling. The time-dependent behavior of PAE adsorption obeyed a mono-molecular layer adsorption as characterized in Langmuir-type expression. The initial increase in PAE adsorption was fast for a few minutes, but it slowed down at longer times as the fiber surface become saturated. The primary apparent rate constants and the maximum adsorption PAE were determined using slow near-equilibrium adsorption kinetics. The secondary apparent rate constants later being required in PAE adsorption simulations were then determined with the model fitting on the initial dynamic adsorption kinetics. The prediction model provided the real-time PAE adsorption behavior on fibers in aqueous solution and showed a good agreement with the experimental data.

Keywords: PAE, adsorption, pulp fiber, wet-strength resin, colloid titration, kinetics

Introduction

Polyamide-epichlorohydrin (PAE) resin appeared on the market in 1960’s as a wet-strength additive and has increased their share of usage in the paper industry at the expense of conventional formaldehyde-based thermosetting polymers such as urea-, phenol- and melamine-formaldehyde resins. Their rapid growth in commercial applications for paper industry was due to a number of reasons including excellent cost effectiveness, wide versatility, and ease of use [1]. The PAE resins generally have 3-hydroxyazetidinim groups in the polymeric structure which are responsible for the reactivity and the cationic character of this PAE resin and enable them to adsorb on negatively charged paper fibers at near-neutral and alkaline pH conditions. This reactive groups contact to cross-link, which causes the resin to cure when the paper is dried and put into storage, finally developing the wet-strength properties on paper [2,3]. The practical aspects of using PAE resins in papermaking have been reviewed by Pahl and Espy [4]. Being highly charged cationic polymers, PAE resins are substantive to negatively charged fibres and are likely to be adsorbed when added to a papermaking furnish. At low dosages there is a steady increase in wet strength, but a point is reached where resin retention starts to decrease as the adsorption sites on the fibres (carboxyl groups) diminish and furnish becomes less negatively charged. In papermaking process, the PAE adsorption by cellulose fibers is one of major importance to produce wet-strength properties of paper and paperboard [5]. Many factors appear to influence adsorption and retention and, consequently, the extent of development of wet strength in the final paper [6]. To effectively control the papermaking wet-end process, it is necessary to understand the adsorption kinetic properties of each additive in the pulp suspension since kinetic effects play an important roll under practical conditions [1]. Extensive kinetic studies on the wet-strength resin adsorption or retention on fibers have been made with melamine and urea resin by Thode and coworkers [7]. They reported that the initial rate of adsorption on beaten sulfite pulp was approximated by a first order mechanism and the activation energies determined were 5.6 kcal/mole and 5.2 kcal/mole for the adsorption of melamine and urea resin acid colloids on fibers, respectively. None of the research report on the adsorption kinetics for PAE resin has, however, been found in the
litteratures. Therefore, the underlying aim of this current work was to investigate the adsorption kinetics of PAE polymers in an aqueous cellulosic fiber solution. Colloid titration method was employed in the determination of the residual concentration of PAE resin in the pulp slurry mixture. A dynamic model was established to simulate the PAE adsorption process. To test the reliability of the model, experimental observations and theoretical fits were compared.

**Experimental**

The pulps used for these experiments were a mixture of 65% LBKP and 35% NBKP slightly beaten to a Canadian Standard Freeness of 500 mL. The wet-strength resin used was a commercial polyamide-epichlorohydrin (PAE) with an average molecular weight of 500000 and particle charge density of 5.0 meq/g. PAE resin sample was diluted to 1.2% solid concentration with de-ionized water before addition to the pulp slurry. The PAE adsorption experiments were conducted with the pulp slurry diluted to 0.5% consistency. The samples taken from every adsorption experiment were then centrifuged for twenty minutes at the rotation rate of 300 rpm. After centrifuge, 10 mL of pure supernatant from each sample was carefully collected for succeeding experimental process. The residual PAE concentrations in solution were then determined using the particle charge detection apparatus (Mutek PCD 03-pH, Mutek Analytic Inc., Germany) whose schematic diagram is illustrated in Figure 1.

In the colloid titration, 0.001N PES-Na (sodium polyethersulfonate) polyelectrolyte solution was used as an anionic standard polyelectrolyte neutralizer. The titrant solution was injected at the flow rate of 0.01 mL per second until the residual PAE in solution was neutralized to the isoelectric point. The sample solution located in the annulus near the cylinder wall and piston walls move back and forth in an oscillating fashion. The pressure created by the piston motion produces an AC current that can be detected by electrodes imbedded in the sides of the cylinder. All measurements were carried out at 20°C and a constant pH of 7.0 with limited contact times to 1200-sec. range. The surface charge of residual PAE in sample solution was estimated from the equation [8]:

\[
\sigma = \frac{(t_b - t_s)F}{V}
\]

where \(\sigma\) is the surface charge of PAE in unit volume of sample (meq/mL), \(t_b\) and \(t_s\) are the blank and sample titration endpoint times (sec.), \(F\) is the PES-Na solution injection rate (meq/sec.), and \(V\) is the volume of sample solution (mL).

**Results and Discussion**

**PAE Adsorption Kinetics**

The kinetics of adsorption of PAE polyelectrolyte on fiber surface has been examined as a function of PAE dosage at neutral pH. Figure 2 shows the time-dependent adsorption curves for three PAE dosages ranging from 0.25 to 1% on oven dry weight of fiber.

The amount of PAE adsorbed onto the pulp surface at all concentrations increases with time, with the majority of PAE being presumably adsorbed within a few minutes. The initial increase is fast, but it slows down at longer times as the fiber surface becomes saturated. It is obvious that all the added PAE finally ends up on the fibers, and that the rate of adsorption increases with raised initial charge of PAE. The results also indicate that the adsorption reaches the equilibrium faster at lower PAE dosages. However, much longer time may elapse before a steady concentration is reached in the solution at all concentrations. Previous adsorption studies of water-soluble polymers on mineral substrates state that the
polymer is either observed or assumed to reach adsorption equilibrium within 1 ~ 2 days for the specific polymer dosages, pH conditions, solid loadings, and shear environments [9]. The PAE is initially adsorbed in a conformation not very different from that in bulk solution [10,11]. It immediately starts to reconform towards an equilibrium configuration, but penetration into the pores in fibers also starts as soon as the PAE has adsorbed onto the cellulosic fibres. This may explain the reason why the PAE adsorption on porous fibers cannot easily reach an equilibrium state. From the patterns of the adsorption behavior as shown in Figure 2, it can be postulated that the PAE adsorption is divided into two stages: the first, initial fast dynamic adsorption stage can be viewed as an electrostatics-favored situation when the diffusion is the rate-limiting step, while the second, slow near-equilibrium slow stage may be the result of rising interface concentration and diminising electrostatic attraction at interface between bulk solution and fiber surface.

**Near-Equilibrium Phase Adsorption Kinetics**

The true equilibrium of PAE adsorption may be reached only after several days (or even several weeks) instead of the few minutes or few hours which are usually sufficient for adsorption of papermaking wet-end additive polymers. This implies that it is very difficult to be certain whether or not true equilibrium of PAE adsorption has been reached at any given time. Because such long periods are involved, we need to arbitrarily establish the apparent equilibrium for polymer adsorption that can be estimated by a theoretical approximation. The adsorption of PAE can be considered as the collision process and rearranging the equation (2), we obtain,

\[
\frac{dN_f^t}{dt} = k_{ads} - \frac{k_{ads}N_f^t}{N_f^\infty} \quad (3)
\]

where \( k_{ads} \) is the primary apparent rate constant for near-equilibrium phase adsorption of PAE on fiber surface. Then a plot of \( dN_f^t / dt \) against \( N_f^t \) should be a straight line of slope \( k_{ads} / N_f^\infty \) and intercept \( k_{ads} \). These kinetic parameters determined for PAE adsorption are summarized in Table 1.

**Dynamic Model for PAE Adsorption**

In the development of prediction model for PAE adsorption on fiber, we considering the initial adsorption of PAE in Figure 2, neglecting the rate of the desorption process and rearranging the equation (2), we also obtain,

\[
\frac{dN_f^t}{dt} = \phi k_{ads}N^s_0\left(1 - \frac{N_f^t}{N_f^\infty}\right) \quad (4)
\]

where all the number concentrations are expressed per unit volume of the suspension. The conservation of the mass requires

\[
N_0 = N_0^0 - N_f^t \quad (5)
\]

Which combined with equation (4) gives

\[
\frac{dN_f^t}{dt} = \phi k_{ads}N^s_0(\lambda_0 - N_f^t)\left(1 - \frac{N_f^t}{N_f^\infty}\right) \quad (6)
\]

And by dividing with \( N_f^\infty \) yields

\[
\frac{d}{dt}\left(\frac{N_f^t}{N_f^\infty}\right) = \phi k_{ads}N^s_0\left(N_0^0 - N_f^t \over N_f^\infty\right)\left(1 - \frac{N_f^t}{N_f^\infty}\right) \quad (7)
\]

\( N_f^t / N_f^\infty \) represents the fractional surface coverage \( \theta \) and \( N_0^0 / N_f^\infty = \lambda_0 \) reflects the ratio between the number of PAE present and the maximum number of PAE that may deposit on the available surface of the fibers, thus

\[
\frac{d\theta}{dt} = k''_{ads}(\lambda - \theta)(1 - \theta) \quad (8)
\]

where the \( k''_{ads} \) is the secondary apparent rate constant for the initial adsorption phase of PAE and the parameter \( \lambda_0 \) is of particular importance in a system containing fewer
Table 1. Kinetic Parameters for PAE Adsorption in Aqueous Fiber Suspension

<table>
<thead>
<tr>
<th></th>
<th>1 % initial PAE</th>
<th>0.5 % initial PAE</th>
<th>0.25 % initial PAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{ads}}$ (sec$^{-1}$)</td>
<td>0.020</td>
<td>0.032</td>
<td>0.036</td>
</tr>
<tr>
<td>$k''_{\text{ads}}$ (sec$^{-1}$)</td>
<td>0.030</td>
<td>0.036</td>
<td>0.038</td>
</tr>
<tr>
<td>$N_f^\infty$ (L$^{-1}$)</td>
<td>1.28×10$^{17}$</td>
<td>6.93×10$^{16}$</td>
<td>3.54×10$^{16}$</td>
</tr>
</tbody>
</table>

PAE polymers that can deposit at maximum coverage. It is not included in the Langmuir analysis [14], where it is usually assumed that there is an excess of adsorbents available for full coverage. It is of interest to note that as $t \to 0$, $\lambda \to 0$ and equation (8) reduces to

$$\theta = k_{\text{ads}} \lambda_0 \delta t \quad (9)$$

Based on the equation (8), a plot of against $(\lambda_0 - \theta)(1 - \theta)$ should be a straight line of slope of $k_{\text{ads}}$. The kinetic parameters for PAE adsorption determined in both the dynamic phase and the near-equilibrium phase are shown in Table 1.

The primary apparent rate constants for PAE adsorption in both initial and near-equilibrium phases decrease as initial charge of PAE increases. This suggests that the PAE-PAE polymeric interaction effects in solution are significant at higher concentration of PAE in unit volume. Theoretical equilibrium for adsorption can also be significantly influenced by the initial charge of PAE. In general, higher equilibrium could be attained at higher PAE concentration. It is interesting to note that somewhat larger values were observed in the secondary rate constants compared to those of the primary ones, and that their differences increased with increasing initial charges of PAE. The values of $k''_{\text{ads}}$ and $N_f^\infty$ obtained here will be used in the theoretical prediction model for PAE adsorption derived in succeeding discussions. The equation (8) on separation of variables and formal integration becomes

$$\int_0^\theta \frac{d\theta}{(\lambda_0 - \theta)(1 - \theta)} = k_{\text{ads}} \int_0^t \frac{dt}{t} \quad (10)$$

After breakdown into partial fractions, integration, and rearrangement of the equation (10), one could obtain the following analytical solution:

$$\theta = \frac{1 - \exp\left[(1-\lambda_0)k_{\text{ads}}t\right]}{1 - \lambda_0^{-1} \exp\left[(1-\lambda_0)k_{\text{ads}}t\right]} \quad (11)$$

which describes the rate of PAE deposition under conditions where the number of PAE polymers present exceeds the number of that can deposit, $\lambda_0 > 1$, as well as where there is a shortage, $\lambda_0 < 1$. In Figure 3, the fractional coverage $\theta$ is shown for different $\lambda_0$ as a function of dimensionless time $\tau$ in order to emphasize the early stage of PAE adsorption. Time $\tau$ is defined as

$$\tau = \frac{t}{\lambda_0 N_f^\infty} \quad (12)$$

The value of $\theta$ in figure (11), however, indicates a relative amount of adsorbed moiety at time, $t$, on the maximum adsorption at a given initial PAE charge. Therefore, it will always vary between zero and unity, even though different initial PAE charges are employed in the PAE adsorption process. In order to obtain an absolute fractional coverage ($\theta_{\text{PAE}}$), we need to modify the equation (11) with the relationship between the absolute fiber coverage with PAE on oven dry weight of fiber ($f_{OD}$) present in solution and adsorption time as:

$$\theta_{\text{PAE}} = \frac{N_f^\infty M\theta}{N_{OD} f_{OD}} \quad (13)$$

where $M$ indicates the average molecular weight of PAE and $N_A$ is the Avogadro’s number. With combining equations (11) and (13), we obtain the modified prediction model as,

$$\theta_{\text{PAE}} (\%) = \frac{N_f^\infty M[1 - \exp\left((1-\lambda_0)k_{\text{ads}}t\right)]}{N_{OD} f_{OD}[1 - \lambda_0^{-1} \exp\left((1-\lambda_0)k_{\text{ads}}t\right)]} \quad (14)$$
To test the reliability of Equation (14), experimental observations and theoretical fits were plotted in Figure (4).

In Figure 4, the data plots are experimental observations while dotted curves are theoretical model outputs obtained from equation (14) with the kinetic parameters of $k_{ads}$ and $N_f^\infty$ available in Table 1. The result indicates that the time-dependent adsorption of PAE in papermaking wet-end can be predictable at high accuracy once the required kinetic parameters are given.

**Conclusions**

The colloid titration experiments were conducted to investigate the adsorption kinetics of PAE on cellulosic fibres suspended in water solution. PAE dosages varied ranging from 0.25 to 1 % on oven dry weight of fiber. The PAE adsorption on fibers obeyed a mono-molecular layer adsorption as characterized in Langmuir-type expression. The PAE adsorption increased with time, with the majority of PAE being adsorbed within a few minutes, but it slowed down at longer times as the fiber surface become saturated. All the added PAE finally ended up on the fibers, and the rate of adsorption increased with an increased initial charge of PAE. The overall PAE adsorption process was considered to have two distinguishable adsorption stages including the initial fast dynamic adsorption phase and the final slow near-equilibrium adsorption one. For the near-equilibrium adsorption kinetics, a simplified Langmuir type adsorption model was used to determine the kinetic parameters including the primary apparent rate constants and the maximum amounts of adsorbed PAE. The secondary apparent rate constants for the initial fast dynamic adsorption kinetics were also determined using a dynamic model developed on the assumption of monolayer molecular adsorption theory. The simulation model for PAE adsorption on fibers not only predicted the real-time PAE adsorption behavior at high accuracy once the kinetic parameters were given, but showed a good agreement with the experimental data.

**References**