# Adsorption Kinetics for Polymeric Additives in Papermaking Aqueous Fibrous Media by UV Spectroscopic Analysis

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The general objective of the present study was to investigate the potential application of the UV spectroscopic method for determination of the polymeric additives present in papermaking fibrous stock solutions. The study also intended to establish the surface-chemical retention model associated with the adsorption kinetics of additives on fiber surfaces. Polyamide epichlorohydrin (PAE) wet strength resin and imidazolinium quaternary (IZQ) softening agents were selected to evaluate the analytical method. Concentrations of PAE and IZQ in solution were proportional to the UV absorption at 314 and 400 nm, respectively. The time-dependent behavior of polymeric additives obeyed a mono-molecular layer adsorption as characterized in Langmuir-type expression. The kinetic modeling for polymeric adsorption on fiber surfaces was based on a concept that polymeric adsorption on fiber surfaces has two distinguishable stages including initial dynamic adsorption phase and the final near-equilibrium state. The simulation model predicted not only the real-time additive adsorption behavior for polymeric additives at high accuracy once the kinetic parameters were determined, but showed a good agreement with the experimental data. The spectroscopic method examined on the PAE and IZQ adsorption study could potentially be considered as an effective tool for the wet-end retention control as applied to the paper industry.

**Key Words :** Spectroscopic analysis, Polymer adsorption, Fiber, Wet-strength resin, Softener

## Introduction

Many different synthetic and natural chemical additives are used in the paper industry for a variety of different reasons during the wet formation process. Typical additives commonly used to improve both the paper properties and the process efficiency include dry strength resins, wet-strength agents, sizing additives, retention aids, drainage aids, fixing agents, dispersing agents, de-foaming agents and slime controllers.[1] Most are used as polyelectrolytic additives with an ionic charge. In the papermachine wet-end, these chemicals interact with individual fibers or one another immediately prior to sheet formation through a serious of physical processes including adsorption, flocculation, conformation and reflocculation.[2] The initial adsorption of the additives on the fibers primarily determines the overall effectiveness of the wet-end chemical treatments. The time-dependent retention/adsorption behavior of papermaking additives in wet-end is, therefore, most important for the understanding of the wet-end aspects of papermaking. It may also serve as a real-time control method. Since the papermaking process is a dynamic one, and the timescales are much shorter than required to reach equilibrium,[3] adsorption kinetic study of polymers is usually more relevant than equilibrium data. Although extensive studies have been conducted on the adsorption of individual species onto the cellulose fibers, much less is known about the adsorption of multi-component polymer solutions where more than one polymeric species are competing for surface sites.[4] One of the major difficulties in the study of competitive adsorption is the analysis of individual species concentration in the multi-component polymeric system.

There are several methods that are commonly used for study of polymer adsorption by the paper industry. Due to ionic nature of most paper chemical additives, charge titration method is widely used.[5] However, this method is time-consuming and may fail to determine the polymer content at very low concentrations.[2] To determine the individual species concentration in a co-ionic dual polymer system, two frequently used methods are radioactive labeling and fluorescence labeling. While these methods were shown to provide valuable information on the competitive adsorption of various polymeric systems,[6,7] they present operational difficulties, and sometimes fail to produce reliable results. For example, besides the safety issues associated with the radioactivity, the accuracy of fluorescence method is limited at low concentration s due to a low fluorescence background which can not be removed even after extensive washing of pulp.[8]

The primary objective of the present study was to establish a quantitative real-time spectroscopic method for the determination of concentration of polymeric additives present in papermaking wet-end stock solutions. The secondary objective was to develop a retention model associated with the adsorption kinetics of polymeric additives onto fiber surfaces. Polyamide epichlorohydrin (PAE) wet-strength resin and an

imidazolinium quaternary (with alkyl substituent groups, IZQ) type softening agent were selected to demonstrate the application of the method. These two polymeric additives are commonly used in commercial tissue manufacture to produce tissue with improved wet strength and softness properties.

## Experimental Section

**Materials.** The pulps used for these experiments were a mixture of 65% bleached hardwood kraft pulp and 35% bleached softwood kraft pulp slightly beaten to a Canadian Standard Freeness of 500 mL. The wet-strength resin used in this study was a commercial polyamide-epichlorohydrin (PAE) with the average molecular weight of 500,000. Its chemical structure is shown in Figure 1.

The softening agent used was a commercial imidazolinium quaternary (methyl-1-tallow-amidoethyl-2-tallow imidazolinium methyl sulfate; IZQ). The typical imidazolinium quaternary structure is illustrated in Figure 2, which is a resonance hybrid between the two extreme structures.[9] The R in the formula refers to the long aliphatic hydrocarbon chain consisting from 11 to 21 carbon atoms. $R_1$, $R_2$ are usually smaller groups, or hydrogen.

The physical properties of PAE and IZQ are summized in Table 1 and 2, respectively.

**Apparatus.** A diode array spectrophotometer (UV-845x, Hewlett-Packard, CA, USA), equipped with a 10 mm silical cell, was used for the spectrophotometric measurements. A
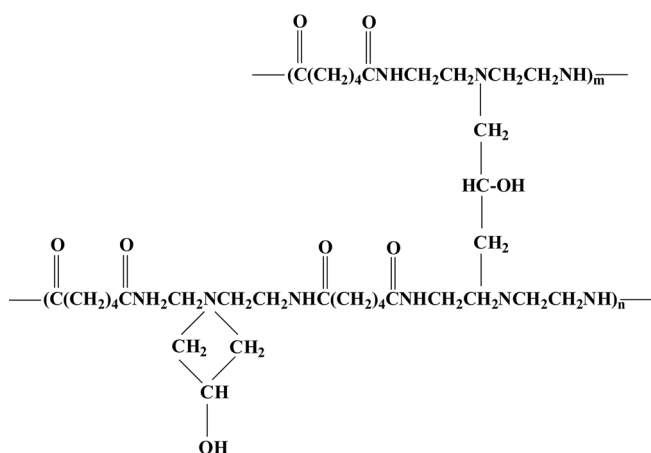
**Table 1.** Physical properties of polyamide-epichlorohydrin (PAE) wet-strength additive, which is the aqueous solution of 12.5 percent solid concentration

| Property | | Property | |
|---|---|---|---|
| Boiling point, °C | 100 | Evaporation rate | Similar to water |
| Freezing point, °C | 0 | Specific gravity | 1.03 |
| Vapor density | Lighter than air | Solids, % | 12.5 |
| pH | 2.8-3.2 | Appearance | Liquid |
| Solubility in water | Miscible | Color | Light amber |

**Table 2.** Physical properties of imidazolinium quaternary (IZQ) softening agent

| Property | | Property | |
|---|---|---|---|
| Boiling point, °C | N/A | Evaporation rate | N/A |
| Melting point, °C | 44-47 | Specific gravity | 1.0 |
| Vapor density | N/A | Flash point, °C | > 93 |
| pH | 4.5-5.6 | Appearance | Viscous fluid |
| Solublity in water | Dispersible | Color | Light tan |

peristaltic pump (RP-1, Raininm Woburn, MA) was used in the experiments for the kinetic adsorption study. The schematic diagram of the experimental apparatus used in the polymer adsorption experiment is illustrated in Figure 3.

**Procedure.** The major flow loop consisted of a 25 mL beaker, a 200 mesh screening chamber, which extracts the liquid from the aqueous pulp slurry, and a UV-Visible optical flow cell. A mesh screen was used to filter out pulp fibers. The filtrate was transferred by a peristaltic pump to a photometric detector for UV/Vis measurement and re-circulated to the beaker. The mixing of pulp suspension was provided by a Teflon-coated magnetic stirring bar (7 mm length and 2 mm width). The rotation speed of the magnetic stirrer was set at 500 rpm. The filter mesh was positioned at the beaker center and 5 mm above the top of the stirring bar. The filtrate was circulated through the optical flow cell of



**Figure 1.** Typical chemical structure of polyamide-epichlorohydrin polymer where m and n are the numbers of repeating unit.
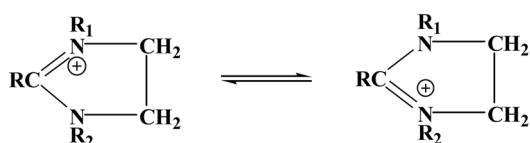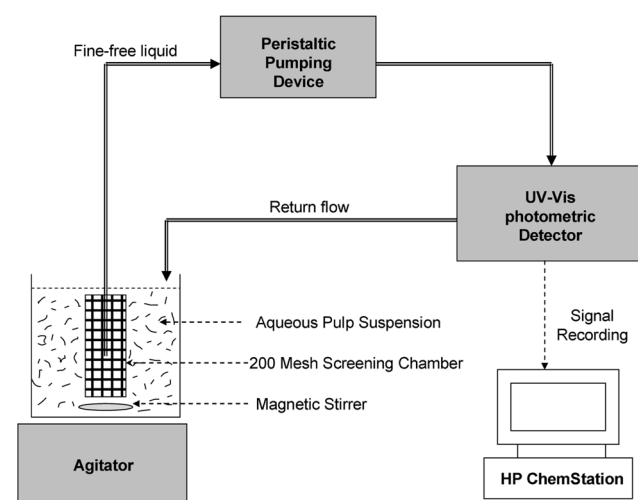


**Figure 2.** Two resonance structures of imidazolinium compound where R refers to the long aliphatic hydrocarbon chain consisting from 11 to 21 carbon atoms and $R_1$ and $R_2$ are smaller groups, or hydrogen.



**Figure 3.** Schematic diagram of experimental apparatus for polymer adsorption study.

the spectrophotometer by the peristaltic pump. The flow rate of the pump was set at 5 mL per minute. The total dead volume of the Teflon tubing and the flow cell was 0.21 mL or 1.05 percent of the solution volume in the beaker. The spectra signals collected by the spectrophotometer had a time lag of 1.3 seconds compared to those in the bulk solution. The HP ChemStation was connected to the spectrophotometer for real-time data collection and analysis. All measurements were carried out at 20 °C and a constant pH of 7.0 up to 250-seconds. In addition, a constant pulp consistency of 0.6% was maintained throughout.

## Results and Discussion

**UV spectra of PAE and IZQ.** A typical UV absorption spectra for the dissolved PAE resin and IZQ tissue softener are illustrated in Figure 4. PAE has a strong absorption in the UV range. A characteristic peak shown at a wave length of 314 nm indicates that the PAE concentration can be easily quantified using UV spectroscopic measurement. The absorption spectrum of IZQ tissue softener in solution, however, shows the absorption over all UV and visible range without a distinguishable absorption peak at a specific wave length. We believe that the absorption resulting from the IZQ tissue softener is caused by light scattering, because of IZQ is only sparingly insoluble in the water.

**Quantifying the concentrations of PAE and IZQ.** The UV absorption was measured for the standard PAE samples at the wave length of 314 nm over the concentration range of 0 to 120 ppm and for the standard IZQ samples at the wave length of 400 nm from 0 to 90 ppm, respectively. Although the absorption contributed by IZQ tissue softener is due to its insolubility in the aqueous solution, it can also be quantified by measuring the turbidity of the solution.[10,11] Figure 5 shows the calibration curves for the solution only containing a single PAE and IZQ, respectively. It is observed that the absorptions at a given wavelength for these compounds are linear to their concentrations within our applicable range
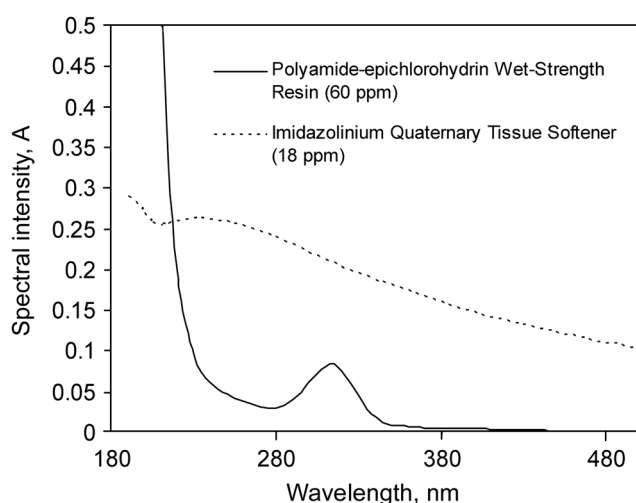
when using a cell with 1 cm optical path-length. This linear calibration suggests that Beer-Lambert Law was applicable to both chemical species at the concentration range considered.[12,13] Therefore, the concentration of the chemical additive can be easily quantified using a spectroscopic method by measuring either the absorption of certain functionalities or turbidity in a single additive solution. The regression coefficients in both cases are 0.99.

**Precision of the method.** A repeatability test of the method was performed using the PAE-pulp solution showed that the relative standard deviation from 5 measurements was less than 5%, indicating that the measurement has a high precision. The UV spectroscopic method developed in this study is very simple and rapid, and overcomes disadvantages of traditional method employed in the paper industry. Due to the capability of collecting accurate data in a relative short period of time, the method has the potential to be utilized as a valuable tool for either a laboratory-scale fundamental research or an on-machine wet-end process control.

**Application to adsorption kinetics.** As mentioned above, in conventional methods used by the paper industry, the real-time measurement of concentration changes in chemical additives has been hindered due to limitations of the analytical methods. In addition, the conventional measurements were invasive, and it is not easy to take samples at short time intervals. In contrast, this method is non-invasive, and can perform a real-time measurement in the papermaking wet-end system. With the calibration method established for the individual and binary component solution, the technique developed in this study can collect spectroscopic data rapidly (every second), and provides important adsorption information, which is unavailable to the study by the conventional methods.

*Adsorption kinetics for PAE and IZQ*: The single component adsorption of PAE wet-strength resin or IZQ softener on fiber was examined as a function of contact time at neutral pH using the spectroscopic method. A fiber consistency of 0.6% was used in all experimental runs. Figure 6 shows an example of time-dependent concentration curves
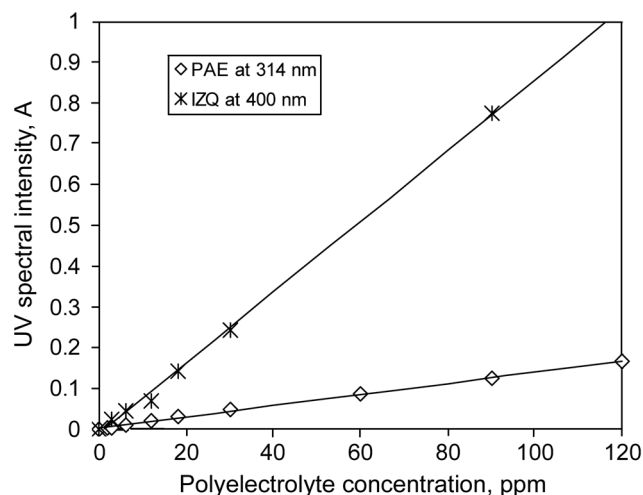


**Figure 4**. Typical UV absorption spectra of PAE and IZQ in solution.



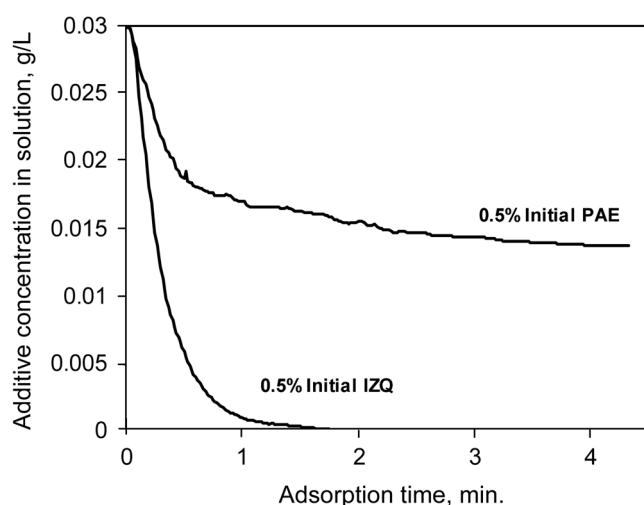**Figure 5**. Calibration curves for PAE and IZQ in standard solution.

**Figure 6**. Time-dependent additive concentrations of PAE and IZQ determined by UV spectroscopic method in fibrous solution.

for one set of initial additive charges of 0.5% PAE and 0.5% IZQ based on oven dry weight of fibers in solution.

The amount of PAE or IZQ adsorbed onto the fiber surface increases with time, with the majority of additives being presumably adsorbed within a few minutes. With prolonged time, more than 90 percent of adsorption was reached for IZQ adsorption on fiber. In PAE adsorption, however, less than 50% adsorption of initial PAE charge was observed. Lower adsorption of PAE compared to that of IZQ could be presumably explained by the difference in the molecular weight of chemical additive used. PAE can be estimated to have about 1,000 times higher molecular weight than IZQ. This large macromolecule of PAE would have a stronger long-range interaction effect between the PAE molecule on fiber surface and that in the bulk solution and among the adjacent molecules adsorbed on fiber surfaces. There may also be an electrical and physical hindrance effect exerted by the adsorbed PAE molecule so that the other approaching PAE molecule would have a lower probability for the contact with a vacant active site on fiber surface. In addition, the PAE is initially adsorbed in a conformation not very different from that in bulk solution. It immediately starts to reconform towards an equilibrium configuration, but penetration into the pores in fibers also starts as soon as the additive has adsorbed onto the cellulosic fibres. This may explain the reason why the macromolecular additive adsorption on porous fibers cannot easily reach an equilibrium state. For the low molecular weight additive such as IZQ, however, the available adsorption area (including fiber surface, microfibrils on fiber surface, and fiber interior) is large enough to reach a high adsorption equilibrium state.[14] Furthermore, IZQ does not seem to take the configuration of high molecular weight polymers on the fiber surface. For the adsorption of ionic surfactants onto an oppositely charged surface, the charged headgroups of the surfactant prefer contact with the surface by electrostatic attraction taking the 'head-on' orientation on the fiber surface.[15] From the shape

of the adsorption curve shown in Figure 5, it can also be postulated that the PAE or IZQ adsorptions are divided into two stages: the first, fast stage can be viewed as an electrostatics-favored situation when the diffusion is the rate-limiting step, while the second, slow stage may be the result of rising interface concentration and diminishing electrostatic attraction at interface between bulk solution and fiber surface.

***Near-equilibrium phase kinetic parameters***: The true equilibrium of additive 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 additive 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 and IZQ can be considered as the collision process between additives with fibers in solution. In the system composed of oppositely charged components it can be assumed that the additive polymers collide only with fibers and upon collision remain attached to the fiber. Assuming Langmuir kinetics,[12] the number of additive polymers on the fiber surfaces at time can be described by

$$\frac{dN_A^s}{dt} = \phi k_{ads} N_A^l N_v^s \left(1 - \frac{N_A^s}{N_{A,\infty}^s}\right) - k_{ads} N_v^s \frac{N_A^s}{N_{A,\infty}^s} \tag{1}$$

where $\phi$ is an efficiency factor, which depends on the ratio of attractive and shear forces.[13] $k_{ads}$ and $k_{des}$ are rate constants for adsorption and desorption, respectively. $N_A^l$ is the number of additive polymers in liquid phase (per unit volume) at time $t$, $N_v^s$ is the total number of vacant sites on fiber surfaces available for the additive polymer adsorption in suspension per unit volume and $N_{A,\infty}^s$ is the maximum number of additive polymers on fiber surfaces at $t = \infty$. Taking only the plateau part of the adsorption of additive polymer in Figure 6 into consideration, neglecting the rate constant value of the desorption process and rearranging the equation (1), we obtain,

$$\frac{dN_A^s}{dt} = k_{ads}' - \frac{k_{ads}' N_A^s}{N_{A,\infty}^s} \tag{2}$$

where $k_{ads}'$ is the primary apparent rate constant for near-equilibrium phase adsorption of additive polymers on fiber surfaces. Then a plot of $dN_A^s/dt$ against $N_A^s$ should be a straight line of slope of $k_{ads}'/N_{A,\infty}^s$ and intercept $k_{ads}'$. These primary kinetic parameters determined for adsorption of two polymeric additives are summarized in Table 1.

***Dynamic retention model for PAE and IZQ adsorption***: In the development of prediction model for PAE adsorption on fiber surfaces, we consider the initial adsorption phase of PAE and IZQ in Figure 6, neglect the rate of the desorption process and rearrange the equation (1) to obtain,

$$\frac{dN_A^s}{dt} = \phi k_{ads} N_A^l N_v^s \left( 1 - \frac{N_A^s}{N_{A,\infty}^s} \right) \tag{3}$$

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

$$N_A^l = N_{A,0}^l - N_A^s \tag{4}$$

where $N_{A,0}^l$ is the number of additive polymers in solution at $t = 0$. Combining equation (3) and equation (4) gives

$$\frac{dN_A^s}{dt} = \phi k_{ads} N_v^s (N_{A,0}^l - N_A^s) \left( 1 - \frac{N_A^s}{N_{A,\infty}^s} \right) \tag{5}$$

and by dividing with $N_{A,\infty}^s$ yields

$$\frac{d}{dt}\left( \frac{N_A^s}{N_{A,\infty}^s} \right) = \phi k_{ads} N_v^s \left( \frac{N_{A,0}^l}{N_{A,\infty}^s} - \frac{N_A^s}{N_{A,\infty}^s} \right)\left( 1 - \frac{N_A^s}{N_{A,\infty}^s} \right) \tag{6}$$

$N_A^s/N_{A,\infty}^s$ represents the fractional surface coverage of additives $\theta_A$ and $N_{A,0}^l/N_{A,\infty}^s = \lambda_0$ reflects the maximum adsorption ratio between the number of additive initially present and the maximum number of additive that may deposit on the available surface of the fibers, thus

$$\frac{d\theta_A}{dt} = k_{ads}''(\lambda_0 - \theta_A)(1 - \theta_A) \tag{7}$$

where the $k_{ads}''$ is the secondary apparent rate constant for the initial adsorption phase of additive polymers and the parameter $\lambda_0$ is of particular importance in a system containing fewer additive polymers than 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 $t \to 0$, $\theta_A \to 0$ and equation (7) reduces to

$$\theta_A = k_{ads}'' \lambda_0 t \tag{8}$$

Based on the equation (7), a plot of $d\theta_A/dt$ against $(\lambda_0 - \theta_A)(1 - \theta_A)$ should be a straight line of slope of $k_{ads}''$. The kinetic parameters for additive adsorption determined in both the dynamic phase and the near-equilibrium phase are shown in Table 3.

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 $k_{ads}''$ and

$N_{A,\infty}^s$ obtained here will be used in the theoretical prediction model for PAE adsorption derived in succeeding discussions. The equation (7) on separation of variables and formal integration becomes

$$\int_0^{\theta_A} \frac{d\theta_A}{(\lambda_0 - \theta_A)(1 - \theta_A)} = k_{ads}'' \int_0^t dt \tag{9}$$

After breakdown into partial fractions, integration, and rearrangement of the equation (9), one could obtain the following analytical solution:

$$\theta_A = \frac{1 - \exp[(1 - \lambda_0)k_{ads}''t]}{1 - \lambda_0^{-1}\exp[(1 - \lambda_0)k_{ads}''t]} \tag{10}$$

which describes the rate of additive polymer deposition under conditions where the number of additive 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 7, the fractional coverage of an additive $\theta_A$ is shown for different $\lambda_0$ as a function of dimensionless time $\tau$ in order to emphasize the early stage of additive polymer adsorption. The dimensionless time $\tau$ is defined as

$$\tau = \phi k_{ads} N_v^s t \tag{11}$$

The value of $\theta_A$ in Figure 7, however, indicates a relative amount of adsorbed moiety at time, $t$, on the basis of the
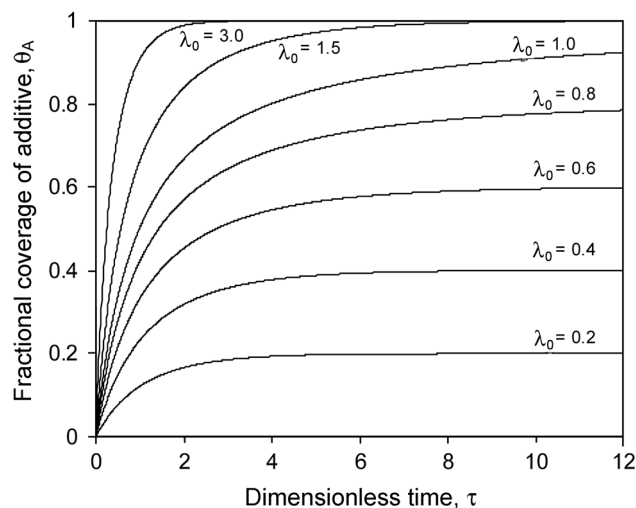


**Figure 7**. Fractional surface coverage $\theta$ as a function of dimensionless time $\tau$ ( $\tau = \phi k_{ads} N_v^s t$ ) for different values of $\lambda_0$ (ratio of number of additive particles present, $N_{A,0}^l$, and maximum number of particles that can deposit, $N_{A,\infty}^s$ ).

**Table 3**. Kinetic parameters for additives adsorption in an aqueous fibrous solution

| Kinetic Parameter | Chemical Additives | |
|---|---|---|
| | Imidazolinium quaternary (IZQ) | Polyamide-epichlorohydrin (PAE) |
| Primary apparent adsorption rate constant ($k_{ads}'$, min$^{-1}$) | 17.30 | 0.03 |
| Secondary apparent adsorption rate constant ($k_{ads}''$, min$^{-1}$) | 5.81 | 2.66 |
| Maximum adsorption ratio ($\lambda_0$) | 1.04 | 2.14 |
| Maximum number of adsorption ($N_{A,\infty}^s$) | $5.24 \times 10^{19}$ | $1.69 \times 10^{16}$ |

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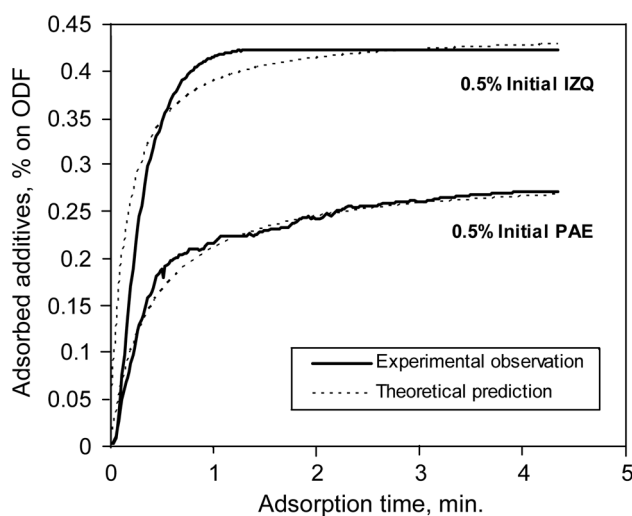
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**Figure 8**. Adsorption of 0.5% PAE and 0.5% IZQ on pulp fibers as a function of time.

maximum adsorption at a given initial additive charge. Therefore, it will always show curves approaching to unity with increasing time, when $\lambda_0$ is greater than 1.0, whatever initial additive charge may be employed. In order to obtain the absolute values expressed in adsorption percentages on fiber surfaces ($\Phi(\%)$), we need to modify the equation (10) using the relationship of the absolute fiber coverage with additives on oven dry weight of fiber ($Wt_{ODF}$) present in solution to adsorption time as:

$$\Phi(\%) = \frac{N_{A,\infty}^s M_A \theta_A}{A_N Wt_{ODF}} \quad (12)$$

where $M_A$ indicates the average molecular weight of an additive polymer and $A_N$ is the Avogadro's number. With combining equations (10) and (12), we obtain a modified prediction model as,

$$\Phi(\%) = \frac{N_{A,\infty}^s M_A [1 - \exp\{(1 - \lambda_0) k_{ads}'' t\}]}{A_N Wt_{ODF} [1 - \lambda_0^{-1} \exp\{(1 - \lambda_0) k_{ads}'' t\}]} \quad (13)$$

To test the reliability of Equation (13), experimental observations and theoretical fits were plotted in Figure 8.

In Figure 8, the noisy solid lines are experimental observations while the dotted lines are theoretical fits obtained from equation (13) with the kinetic parameters of $k_{ads}''$ and $N_{A,\infty}^s$ available in Table 3. The result indicates that the time-dependent adsorption of PAE in papermaking wet-end can be predictable at high accuracy once the kinetic parameters for each polymeric adsorption condition are determined.

## Conclusion

UV absorption spectroscopic analysis has enabled us to determine the time-dependent concentration of polyamide-epichorohydrin (PAE) wet strength resin and imidazolinium quaternary (IZQ) softening agents commonly used in tissue

production industry. A single polymer additive in fiber solution could be easily determined by a simple linear calibration method for PAE and IZQ at the wave length of 314 and 400 nm, respectively. The adsorption of additives increased with time, with the majority of them being adsorbed within a few minutes, but it slowed down at longer times as the fiber surface became saturated. IZQ showed faster and higher adsorption compared to PAE. The time-dependent behavior of polymeric additive obeyed a mono-molecular layer adsorption as characterized in Langmuir-type experession. The overall additive adsorption process was considered to have two distinguishable adsorption states including the initial fast dynamic adsorption phase and the final slow near-equilibrium adsorption one. For the near-equilibrium adsorption kinetics, a simplified Langmuir model was used to determine the kinetic parameter including the primary apparent rate constants and the maximum amounts of adsorbed additives. The secondary apparent rate constants for adsorption were developed on the assumption of monolayer molecular adsorption theory. The simulation model for additives adsorption on fibers could predict not only the real-time additive adsorption behavior at high accuracy once the kinetic parameters were given, but show a good agreement with the experimental data. The spectro-scopic method examined on the PAE and IZQ adsorption study could potentially be considered as an effective tool for the wet-end chemical retention control as applied to the paper industry.

## References

1. Robert, J. C. *Paper Chemistry*, 2nd ed.; Chapman & Hall: New York, 1991; p 64.
2. Scott, W. E. *Principles of Wet End Chemistry*; TAPPI Press: Atlanta, 1996; p 111.
3. Most, D. S. *The Sorption of Certain Slash Pine Hemicellulose Fractions by Cellulose Fibers*, Doctor's Dissertation; The Institute of Paper Chemistry: Appleton, Wisconsin, 1957; p 127.
4. Chang, S. H.; Ryan, M. E.; Gupta, R. K. *J. Appl. Polymer Sci.* **1991**, *43*, 1293.
5. Strazdins, E. *Proceedings of 1992 TAPPI Papermaker Conference*; Nashville, TN, 1992; p 479.
6. Tanaka, H.; Swerin, A.; Odberg, L.; Park, S. B. *J. Pulp Paper Sci.* **1997**, *23*, 359.
7. Tanaka, H.; Swerin, A.; Odberg, L.; Park, S. B. *J. Pulp Paper Sci.* **1999**, *25*, 283.
8. Falk, M. L.; Odberg, L.; Wagberg, L.; Risinger, G. *Colloids and Surfaces* **1989**, *40*, 115.
9. Takano, S.; Tsuji, K. *J. Am. Oil Chem. Soc.* **1983**, *60*, 870.
10. *Water*, Annual Book of ASTM Standard, Part 31; American Society for Testing and Materials: Philadelphia, PA, 1976; D516-68, Method B, p 430.
11. Greenbreg, A. E.; Taras, M. J.; Rand, M. C. *Standard Methods for the Examination of Water and Wastewater*, 14th ed.; Publication Office of American Public Health Association: Washington, 1976; Method 427C, p 496.
12. Atkins, P. W. *Physical Chemistry*, 2nd ed.; W. H. Freeman and Company: San Francisco, 1982; p 605.
13. Martens, H.; Meas, T. *Multivariate Calibration*; John Wiley: New York, 1989; p 190.
14. Alince, B. *J. Appl. Polymer Sci.* **1990**, *39*, 355.
15. Connor, P.; Ottewill, R. H. *J. Colloid Interf. Sci.* **1971**, *37*, 642.