

A Chemometric Aided UV/Vis Spectroscopic Method for Kinetic Study of Additive Adsorption in Cellulose Fibers

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ABSTRACT

This paper describes a technique combining chemometrics with UV spectroscopy for the determination of the concentrations of two tissue additives (i.e., wet strength and softening agents) in a cellulose fiber containing solution. In single agent solutions, the concentration of the additive can be measured by UV spectroscopy at the wavelength where the species having absorption. For a binary (i.e., containing two additives) solution system, the spectral characterization is very complicated. However, if aided by a chemometrical calibration technique, each additive in the binary solution can be quantified simultaneously. The present method is very rapid and simple, it can easily perform a continuous measurement in the changes in the additives' concentration after fiber addition, and therefore this becomes a valuable tool for the adsorption kinetics study of chemical additives onto the cellulose fibers. The time-dependent adsorption behaviors of the wet-strength, softening agent, and their both on fiber were also presented.

Keywords: UV/Vis, spectrophotometric, absorption, additives, kinetics, adsorption, fibers.

INTRODUCTION

Polymers are widely used in the papermaking for various purposes such as charge neutralization, retention, drainage, debonding and strength development [1-2]. In order to be effective in improving sheet properties, the additives must first adsorb onto the pulp fibers. The study of adsorption of paper additives is important to generate understanding of the interaction of specific polymer with cellulose fiber, and to serve as a guide for the additive's practical application in the manufacturing process. Since the papermaking process is a dynamic one, and the timeframes is much shorter than that to reach equilibrium [3-4], the adsorption kinetic study of polymers is usually more relevant. 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 [5-9]. 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 in the chemical adsorption study by the paper industry. Due to cationic nature of most paper chemical additives, charge titration method is widely used in the chemical additive absorption study [10,11]. However, besides some variables that are difficult to control [12], this method is time-consuming and may fail to determine the

polymer content at very low concentrations. To determine the individual species concentration in a binary 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 [13-14], they present operational difficulties, and will fail to produce reliable results under certain circumstances. For example, the uncertainties are involved in the radioactive method besides the safety issues, and the accuracy of fluorescence method is limited under low concentration due to a low fluorescence background which can not be removed even after extensive washing of pulp [15].

In this work, we have developed a simple and rapid method for spectroscopically quantifying the additive concentration in the process solutions. Two commercial additives, Kymene[®]1500 and Softrite[®]7516, were selected to demonstrate the application of the method. They are commonly used as wet strength resin and debonding agent, respectively, in the tissue making for improving the wet strength and softness properties of the product.

EXPERIMENTAL

Apparatus

A diode array spectrophotometer (UV-8453, Hewlett-Packard, CA, USA), equipped with a 10 mm silica flow cell, was used for the spectrophotometric measurements. A peristaltic pump (RP-1, Raininm

Woburn, MA) was used in the experiments for the kinetic absorption study.

Chemicals and materials

The wet strength resin used in this study was Kymene® 1500 (Hercules Inc., Wilmington, DE), a polyamide-epichlorohydrin resin. The average molecular weight was about 500,000. The debonder used is Sofrite® 7516 (Southwest Engineers Paper Science, Slidell, LA). Its active chemical component was methyl-1 tallow-amidoethyl-2-tallow imidazolinium methyl sulfate.

Experimental procedures

The chemical adsorption experiments were conducted with a flow loop. The flow loop consisted of a peristaltic pump tubing and connectors, a 25mL beaker, a net filter of 200 mesh, which was capable of separating the fibers from the chemical solution, and a UV/Vis optical flow cell. Accurately weigh about x amount of pulps and add it in a 25mL beaker where contains 20mL of solution, in which the fiber consistency should be below 0.6 percent. A good mixing of the pulps and chemicals in beaker was obtained by magnetic stirring. All UV/Vis measurements were continuously performed over the whole UV/Vis range by the spectrophotometer equipped with a HP ChemStation for real-time data collection and analysis.

RESULTS AND DISCUSSIONS

Quantifying analysis of Kymene® 1500 and Sofrite® 7516

Since Kymene® 1500 has a distinguished absorption peak at around 314 nm, while Sofrite® 7516 has the absorption over all UV and visible range, thus they can be quantified spectroscopically although it is actually measure the turbidity for Sofrite containing solution [16-17] due to its insolubility in the aqueous solution.

In the Fig. 1, it shows the calibration curves for the solution only containing a single Kymene® 1500 or Sofrite® 7516, respectively. It is observed that the absorption at a given wavelength for these compounds is linear to the their concentrations within our applicable range when using a cell with 1 cm optical path-length. 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 greater than 0.998.

Chemometric aided quantifying analysis for the two additives solution

The spectral behaviors of the binary species solution containing insoluble species are complicated. In this case, the data indicated that the spectral absorption of the mixture solution did not have simple spectral additivity, i.e., the spectral absorption at a given wavelength was not simply the sum of the absorption of two individual components in the solution. We have conducted the

testing based on a set of binary solutions of Kymene® 1500 and Sofrite® 7516, and measured their absorption at 314 nm. The results showed that the calculated absorption by additivity was consistently higher than that actually measured. Therefore, the calibrating methods based on Beer's Law (such as the dual-wavelength method) failed to quantify the individual additive's concentration in such a binary solution system.

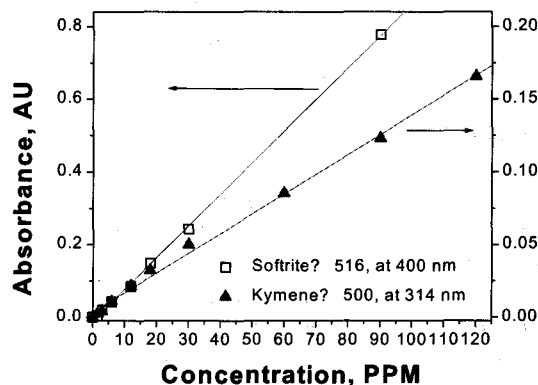


Figure 1. Calibration curves for single component solution system.

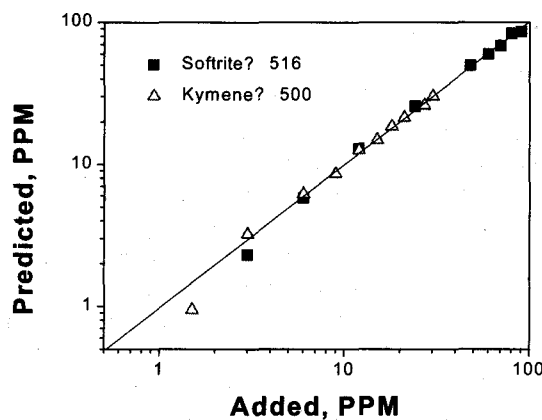


Figure 2. The PLS model prediction for the solution containing two components.

Chemometrics [18-19] is developed for solving complex calibration problems in process analytical chemistry. Multivariate partial-least-square (PLS) analysis is one of the most frequently used technique in chemometrics. PLS is a mathematical algorithm for solving complex multivariable linear relationships. The detailed description of the PLS algorithm is rather complicated and can be found in the tutorial by Geladi and Kowalski [20] and in other literature [21-22].

In this paper, we will mainly demonstrate the PLS application procedures for the quantifying additive concentrations in the binary system.

In PLS method, a calibration database needs to be

built using a set of solutions from the same source of the sample solution, but varying in the species concentrations. Then, the spectra of these solutions are measured by the spectrophotometer. Based on the species concentration data and the corresponding spectral signals, PLS calibration model can be obtained by the chemometric software. In this work, we made 10 standard samples solutions with varied Kymene®1500 and Softrite®7516 concentrations that covering the application range. The spectral signals in the measurement for each solution are collected from 190 to 400 nm. Then, both concentration and spectral signal data are input in a commercial chemometric software (SIMCA, Demo 6.X) to generate a calibration model. With the spectral signals measured on the unknown solutions, the model can predict the species concentrations in the unknown solutions.

Measurement precision of the method

A repeatability of the spectroscopic measurement was performed using the solution of a single chemical additive (Kymene®1500). It was found that the relative standard deviation from 5 measurements was less than 5 %, indicating that the measurements were very repeatable.

As shown in Fig. 2, an excellent prediction ($R^2=0.998$) for the concentration of the individual additives in the mixture can be achieved in the application.

Applications

As mentioned above, in traditional methods used by the paper industry, the adsorption kinetics study of chemical additives on fibers is hindered due to limitations of various analytical methods. In addition, the traditional adsorption techniques are invasive, and it is not possible to gather samples at short time intervals. In contrast, this method is non-invasive, and can perform a real-time measurement over the fiber system. With the calibration method established for the individual and binary component solution, the technique developed in this study can gather spectroscopic data rapidly (every second), and provides important adsorption information, which is unavailable to the study by the traditional methods.

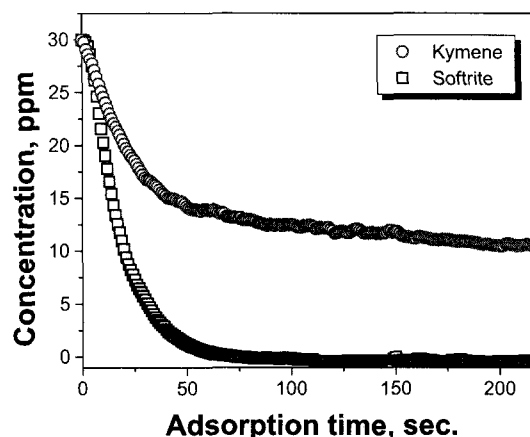


Figure 3. Concentration changes in the single additive solution system. (Fiber consistency = 0.6 %).

Adsorption behavior in a single additive solution system.

The kinetic adsorption behavior of Kymene®1500 and Softrite®7516 were studied separately. A fiber consistency of 0.6 percent was used in the all experiments. The pH of the fiber solution was 7.5 ± 0.1 , and the experiments were performed at 20°C . As shown in Fig. 3, the Softrite®7516 in the solution (starting concentration is 30 ppm) can be completely consumed within 2 minutes at the given process conditions. In comparison, only about 60 % of Kymene®1500 in the solution was consumed in the same period of time, and a slowly decreasing Kymene®1500 concentration in the bulk solution was observed.

Adsorption behavior in the two additives solution system.

The additive adsorption profiles onto the fibers in the mixture solution are shown in Fig. 4. Different from what observed in the single additive system, especially for Softrite®7516, the concentration decrease for each additive in the mixture solution was reduced. We believe that it is a result due to the competing adsorption behavior between two additives on the given area of the fiber surface.

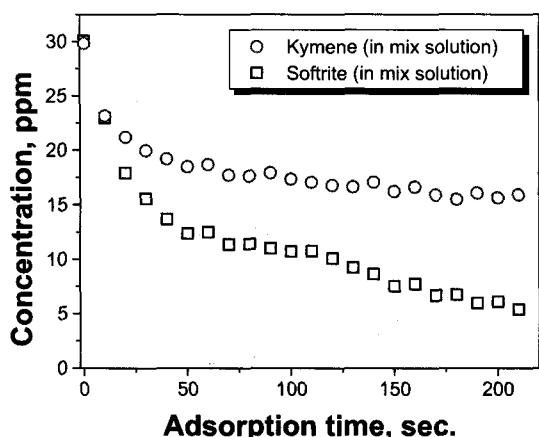


Figure 4. Concentration changes of additive in the binary solution system. (Fiber consistency = 0.6 %.)

CONCLUSIONS

A spectroscopic method has been developed for the determination of two commercial chemical additives (Kymene[®]1500 and Sofrite[®]7516) in the papermaking solution. With help of PLS calibration technique, we are able to analyze two components in the mixture solution system. The present method can perform real time measurements for the additives in the fiber solution during the adsorption. It is very simple, rapid and non-invasive, and has the potential to be utilized as a valuable tool for the adsorption kinetics study of chemical additives onto the cellulose fibers.

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