Development of Visible Light Absorption Measurement for Concentrated Dye Solution based on Attenuated Total Reflection Technique and Improvement on its Analysis Method

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Abstract

An absorption measurement working in ATR (Attenuated Total Reflection) mode has been design for characterization of concentrate dye solution. The system consists of a visible light system as polychromatic wave source, an ATR plate made up from glass or polymer, a spectrometer with a CCD detector. The system is connected to a computer for measurement and data processing. Some commercial inks measured by this ATR system showed absorption spectra which are in agreement with the color of the inks. The absorption parameter will be determined from the incident and reflection beam intensities measured at incident angle larger than the critical angle. We have also carried out Poynting vector analysis and we will show that the energy flow in the normal direction of the interface is not zero. The energy flow, however, decreases along the normal direction of the interface, indicating energy loss due to light absorption in the sample medium. The amount of energy loss depends on the attenuation index or absorption parameters, which is important for formulating the relation between the measured intensities and absorption parameters.

Keywords: Attenuated total reflection (ATR), Total internal reflection, Absorption, Evanescent wave, Optical sensor, Poynting vector

1. Introduction

Attenuated total reflection (ATR) is a phenomenon that is basically similar with total internal reflection (TIR), but the reflection beam is subjected to attenuation due to the absorption of the evanescent wave. In both TIR and ATR case, the evanescent wave is created when a light beam coming from a high refractive index medium into the second medium with lower refractive index (that is, $n_1 > n_2$) at the incident angle larger than the critical angle ($\theta_i > \theta_c$)¹⁾. The evanescent wave penetrates into the second medium within the range of sub-micron. In ATR case, the evanescent wave will be absorbed by absorbing molecules inside the second medium. ATR is therefore often used for surface analysis of thin layer of some materials¹⁻⁴⁾.

The quantitative analysis methods used in ATR spectroscopy are commonly based on Harrick's method, which employ Fresnel formula for non-absorbing medium case combined with a semi-empirical parameter called as effective thickness (d_{eff})¹⁾. This parameter represents the effective penetration depth of evanescent wave inside the second medium. The method is, however, applicable only for weak light absorption case or low absorber molecule concentration case. This restriction hindered further applications of ATR spectroscopy. There is only limited number of studies on quantitative analysis which correlate the absorption parameters and reflectance intensity^{2,3,9)}. Such kind of study is

important to analyze ATR data for more general case, including strong light absorption or high concentration of absorber molecule cases. In this paper, we present our research work in developing a modular ATR spectroscopy system in visible light regime for the measurement of highly concentrated dye solution and its analysis method.

2. Instrumentation and Methodology

ATR system developed here is consisted of a halogen light source, an ATR plate on a rotating stage and a portable CCD spectrophotometer (USB-2000, Ocean Optics) that is connected to a personal computer for the measurement of the reflection light spectrum. Schematic diagram of this measurement system is shown in Figure 1. The CCD spectrophotometer used here is a unique combination of technologies of 2-MHz analog-to-digital (A/D) converter, programmable electronics, a 2048-element CCD-array detector, and a high-speed USB 2.0 port. The size of this spectrophotometer is about 89 mm × 63 mm × 34 mm with total weight of about only 190 grams. This combination of technology is able to measure light spectrum in a couple of ten milliseconds within the spectral range of about 350-900 nm and spectral resolution up to 0.35 nm (FWHM).

ATR plates used in this work were made from poly(methyl-*m*-acrylic) materials shaped in some geometrical forms, as shown in Figure 2. An arrangement of lens was carefully set-up between the

light source and ATR plate to produce a paraxial beam, so that the plane wave approximation in the analysis is still acceptable. This condition is also necessary for minimizing the light dispersion effect. Figure 3 shows the incident and reflected light beam propagation in a hemi-cylinder ATR plate.

Figure 1. Schematic diagram of the ATR Vis-spectroscopy system developed in this work.

Figure 2. Typical shapes of some ATR plates made from poly-acrylic.

Figure 3. The propagation of visible light beam from a halogen light source inside a hemi-cylinder ATR plate.

The energy flux in the second medium (the absorbing medium) was evaluated by calculating the Poynting vector by taking into account complex dielectric constant or index refraction for the second medium. The simulation result of reflectance (R) spectrum using Fresnel formula, at $\theta_1 > \theta_c$, shows a dip similar with the imaginary part of dielectric constant of the second medium, which can be associated with the absorption of evanescent wave²⁾.

However, according to this formula, the absorption is implicitly considered to take place only at the interface. If there is also energy loss inside the evanescent wave region, the measured reflectance will be different than the spectrum calculated from Fresnel formula, particularly in special case such as in a layer with inhomogeneous absorber molecule distribution. In this work, Poynting vector analysis was used to evaluate the loss of energy flow depending on the absorption parameters of the second medium.

3. Results and Discussion

Light absorption in UV-visible range is commonly originated from electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular (LUMO), such as π - π^* transition in most of small organic molecules with π -bonding. In semiconductor materials, the corresponding transition is related to electron excitation from valence band to conduction band. Light absorption in infra red region, on the other hand, is usually related to molecular vibration excitation. The strength of light absorption can be expressed by absorption constant $\alpha(\lambda)$, extinction coefficient constant $\epsilon(\lambda)$, or complex dielectric constant $\kappa(\lambda)$, where the relationship among those constants is given by

$$\alpha(\lambda) = \epsilon(\lambda) c = \frac{4\pi}{\lambda} \kappa(\lambda) \quad (1)$$

with c is the concentration of molecule absorber. In absorption measurement using transmission configuration, the absorbance (A) can be obtained from Beer-Lambert law:

$$A = 2.303 \log \left(\frac{I}{I_0} \right) = \alpha d = \epsilon c d \quad (1)$$

where I is the transmitted light intensity and I_0 is the incident light intensity. In this configuration, with the assumption of very small reflectance (R), we have $A+T=1$, where T is the transmittance.

Figure 4. Evanescent wave at the medium boundary penetrating into the second medium (sample layer)

In ATR spectroscopy, we measure the reflection light intensity, instead of the transmission light intensity, at $\theta_1 > \theta_c$. In such condition, the evanescent wave is created along the interface between the ATR plate (n_1) and sample layer (n_2), as shown in Figure 4. If the sample layer is a non-absorbing medium, we will have a TIR condition,

namely $R=1$ and $T=0$. If the sample layer is an absorbing medium, we will have an ATR condition, namely $R < 1$. In most analysis methods, we accept that $R+T+A=1$ must be obeyed, but there is still a lack of analytical model to determine absorption parameters straightly from the ratio of the measured intensities such as given by Beer-Lambert law.

Figure 5. The light absorption intensity (vs. wavelength) from sample testing of (a) red, (b) green and (c) blue color ink liquid.

Figure 6. Evanescent wave formation in TE mode, that is, when the electric field E is polarized perpendicular to the incident plane (x - z plane).

As a preliminary experimental works, we tried to measure the absorption of some commercial ink liquid. For the absorption measurements in transmission configuration, the ink liquid must be placed in very thin cell or previously diluted by transparent solvent. On the other hand, using this ATR system, we just simply covered the ATR plate with the ink or dip the plate into the ink liquid. Figure 5 shows the measured light absorption intensity (vs. wavelength) of (a) red, (b) green and (c) blue color ink liquid, which are plotted using eq. (2). In this work, the absorption is interpreted to be originated not only from the light absorption at the boundary, but also the light absorption as the evanescent penetrates into the sample medium. In order to understand this physical picture, we calculated the Poynting vector of this evanescent wave. Figure 6 illustrates the electromagnetic plane wave propagation at the boundary with transverse electric (TE) propagation mode. The incident, reflected and evanescent waves can be expressed as following:

$$\begin{aligned}\vec{E}_1 &= E_{1y} \hat{y} = E_{10} e^{i(\omega t - (k_{1x}x + k_{1z}z))} \hat{y} \\ \vec{E}_1' &= E_{1y}' \hat{y} = E_{10}' e^{i(\omega t - (k_{1x}'x + k_{1z}'z))} \hat{y} \\ \vec{E}_2 &= E_{2y} \hat{y} = E_{20} e^{i(\omega t - (\tilde{k}_{2x}x + \tilde{k}_{2z}z))} \hat{y}\end{aligned}\quad (2)$$

where $\tilde{k}_2 = k_0 \tilde{n}_2$ is the wave propagation constant in the second medium, and $\tilde{n}_2 = n_2 - i\kappa$ is complex refractive index.

The projection of $\tilde{k}_2$ at the boundary condition, namely $\tilde{k}_{2z}$, can be calculated from

$$\tilde{k}_2 \cos \theta_2 = \tilde{n}_2 \left(\frac{2\pi}{\lambda_0} \right) \cos \theta_2 \quad (3)$$

At $\theta_1 > \theta_c$, because $n_1 > n_2$, we have only pure imaginary value of $\cos \theta_2$ in the TIR case. The value of $\cos \theta_2$, however, becomes a complex number in the ATR case, which is given by

$$\cos \theta_2 = \sqrt{1 - \sin^2 \theta_2} = -i \sqrt{\frac{n_1^2}{\tilde{n}_2^2} \sin^2 \theta_1 - 1} \quad (4)$$

Here, at $\theta_1 > \theta_c$, the complex $\tilde{k}_{2z}$ can be rewritten in the following expression:

$$\begin{aligned}\tilde{k}_{2z} &= -i \left(\frac{2\pi}{\lambda_0} \right) \sqrt{\text{Re}^{i\phi}} \\ &= -i \left(\frac{2\pi}{\lambda_0} \right) D e^{i\phi} \\ &= \frac{2\pi}{\lambda_0} D (\sin \phi - i \cos \phi)\end{aligned}\quad (6)$$

where

$$\begin{aligned}
A &= D^2 \cos 2\varphi = n_1^2 \sin^2 \theta_1 - n_2^2 + \kappa^2 \\
B &= D^2 \sin 2\varphi = 2n_2 \kappa \\
R &= D^2 = \sqrt{A^2 + B^2} \\
2\varphi &= \phi = \tan^{-1} \frac{B}{A}
\end{aligned} \quad (5)$$

The evanescent wave becomes

$$E_{2y} = E_{20} e^{i\left(\omega t - k_{1x}x - \left(\frac{2\pi}{\lambda_0} D \sin \varphi\right)z\right)} e^{-\frac{z}{\delta}} \quad (6)$$

where

$$\delta = \frac{\lambda_0}{2\pi D \cos \varphi} \quad (7)$$

We can see clearly now that, if the second medium is an absorbing medium ($\kappa \neq 0$), the evanescent wave seems propagating not only in x -direction, but also in the z -direction with attenuated amplitude. It should be noted that the wave propagation in z -direction disappears if the second medium is non-absorbing medium, namely $\kappa = 0$, which is the TIR case.

The time averaged energy flux density of the incident wave $\langle \vec{S}_1 \rangle$ can be calculated from

$$\begin{aligned}
\langle \vec{S}_1 \rangle &= \frac{1}{2} \text{Re} \left[\vec{E}_1 \times \left(\frac{i}{\mu\omega} \vec{\nabla} \times \vec{E}_1 \right)^* \right] \\
&= \frac{1}{2} \text{Re} \left[\vec{E}_1 \times \frac{-i}{\mu\omega} (ik_{1z}\hat{x} - ik_{1x}\hat{z})^* E_{1y}^* \right]
\end{aligned} \quad (10)$$

that is

$$\langle \vec{S}_1 \rangle = \frac{E_{10}^2}{2\mu\omega} [k_{1x}\hat{x} + k_{1z}\hat{z}] \quad (11)$$

By the same method, the time averaged energy flux density of the reflection light $\langle \vec{S}_1' \rangle$ is given by

$$\langle \vec{S}_1' \rangle = \frac{1}{2} \text{Re} \left[\vec{E}_1' \times \left(\frac{i}{\mu\omega} \vec{\nabla} \times \vec{E}_1' \right)^* \right] = \frac{E_{10}^2}{2\mu\omega} (k_{1x}\hat{x} - k_{1z}\hat{z}) \quad (12)$$

Using the wave function given by Eq. 8, the average energy flux density of evanescent wave $\langle \vec{S}_2 \rangle$ is

$$\begin{aligned}
\langle \vec{S}_2 \rangle &= \frac{1}{2} \text{Re} \left[E_{2y} \hat{y} \times \left(\frac{i}{\mu\omega} \vec{\nabla} \times \vec{E}_2 \right)^* \right] \\
&= \frac{E_{20}^2}{2\mu\omega} \left(e^{-\frac{2z}{\delta}} \right) \text{Re} \left[\left\{ \left(\frac{2\pi}{\lambda_0} D \sin \varphi \right) \hat{z} + k_{1x} \hat{x} \right\} - i \frac{1}{\delta} \hat{z} \right]
\end{aligned} \quad (8)$$

or

$$\langle \vec{S}_2 \rangle = \left(\frac{E_{20}^2}{2\mu\omega} \right) e^{-\frac{2z}{\delta}} \left\{ k_{1x} \hat{x} + \left(\frac{2\pi}{\lambda_0} D \sin \varphi \right) \hat{z} \right\} \quad (14)$$

Therefore, the average energy flux density passing through the interface in z -direction is

$$S_{2z} = \langle \vec{S}_2 \cdot \hat{z} \rangle = \left(\frac{E_{20}^2}{2\mu\omega} \right) \exp\left(-\frac{2z}{\delta}\right) (D \sin \varphi) \quad (9)$$

In contrast to the TIR case ($\kappa=0$), where $S_{2z} = 0$, in this ATR case $S_{2z} \neq 0$. That is, there is energy flowing through the interface. As indicated in Figure 7, in the case of weak absorption the energy flow is small such that the penetration depth is large. With the increasing of the absorption constant, the amount of energy flow also increases and the penetration depth becomes smaller as the consequence of the absorption of the evanescent wave. This energy flow is not taken into account in Harrick's model, so that is why the Harrick's model is considered applicable only for very small κ case.

Figure 7. Plot of the average energy flux passing through the second medium normal to the interface (S_z) for various attenuation indexes (κ).

4. Conclusion

A simple ATR spectroscopy system for visible light region has been built using a compact CCD spectrophotometer and polymer ATR plate. The absorption spectra of commercial color ink liquids measured by that system show absorption band which are in agreement with the appearances of their colors. It, however, remains problems for determining the attenuation index (κ) from the measured intensity. Preliminary study on Poynting vector analysis shows that there is a flow of energy in the second medium in normal direction of the interface. This means that the evanescent wave propagates not only along the boundary but also propagates normal to the interface, which is interpreted as the consequence of the light absorption of the evanescent wave inside the second medium. With the increasing of attenuation index (κ), the amount of energy flux passing through the interface also increases followed by shortening of penetration depth. This understanding, which is often disregarded in most ATR analysis methods, is very important to formulate the relationship among the

measured incident, reflection intensities and absorption parameters in ATR case in the next work.

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