DETECTION OF DYE MOLECULES IN SOLUTION USING SURFACE PLASMON RESONANCE TECHNIQUE

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ABSTRACT

Surface plasmon resonance technique has been utilized as a sensitive optical sensor for detection of dye molecule in water. Three dye solutions were chosen for this study, such as methylene blue, rhodamine B and rhodamine 6G. All samples were prepared by dissolving dye powder in distilled water and the solution was diluted several times to produce sample solutions in the range of 0.001 to 0.01 mol/L. The shift of SPR angle ($\Delta\theta_{spr}$) was monitored and characterized as sensor sensitivity and responsivity. The kinetic behaviour of the dye molecules was also discussed.

INTRODUCTION

Surface plasmon resonance (SPR) spectroscopy is a powerful tool for the real-time characterization of a solid/liquid interface. [1,2]. Surface plasmons are collective oscillation of free electrons at an interface between a thin metal film and a dielectric medium. The SPR technique typically involves the optical excitation of surface plasmon polariton waves on a gold film employing the Kretschmann configuration. Reflectivity is measured as a function of the incident angle [1]. The change in the surface results in a shift in the SPR angle in an attenuated total reflectance (ATR) curve. This is because SPR is extremely sensitive to the dielectric constant of the medium immediately adjacent to the metal film. Adsorption of molecules onto the metallic film or conformational changes in the adsorbed molecules can be accurately monitored by optical method [2].

The power of an optical sensor experimental approach in which one of the interacting molecules (the dielectric sample) is free in solution and gold film as a sensor surface is the formation and decomposition of the dielectric sample/gold can be monitored and yielding kinetic data in real time [3]. This technique can be used to monitor the interactions of an analyte and a metal on the surface without the need to label the reactant. The availability of real-time SPR kinetic data provides the possibility of understanding the mechanism of the chemical or physical binding events for surface reaction [2, 3].

Gold is a flexible and simple system that permits the interfacial properties of a metal substrate to be tailored for a well designed functional surface. An attempt was made to identify the adsorption mechanism and kinetics but an approximation was required

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because the direct observation of surface change was impossible. We recently investigated the SPR technique as a metal solution sensor in an aqueous phase. A gold substrate is used as the sensing layer and the electric field near the surface served as a probe. In this study, SPR was used to examine the adsorption of dye solution to a gold thin film surface at the molecular level. SPR technique was found to be useful in identifying the selective adsorption to a functionalized surface and in analyzing the concentration of dye solution in distilled water.

MATERIALS AND METHOD

The active medium used in this study is gold (99.99%). The dye samples are methylene blue, rhodamine B, and rhodamine 6G. Gold thin film (thickness ~50 nm) was deposited onto glass cover slip using sputtering technique (Polaron SC-7640). The glass cover slip with gold thin layer was then attached to one surface of 60º prism using index matching oil. methylene blue was prepared by dissolving a certain amount of methylene blue into distilled water diluted several times to produce the solution concentration of (0.001 – 0.010) mol/L. Similar procedure was applied in preparing Rhodamine B and Rhodamine 6G samples. The sample was then injected into a small cell (volume = 3.31 cm^3) which directly attached to the gold thin film by mechanical means.

The surface plasmon resonance measurement was carried out by measuring the reflected He-Ne laser beam (632.8 nm, 5 mW) as a function of the incident angle. Figure 1 showed the surface plasmon experimental setup used in the present work. It consist of a He-Ne laser and an optical table with a rotation resolution as good as 0.001º. The reflected beam was detected by a sensitive photodiode and the signal was consequently recorded and processed by a lock-in-amplifier (SR 530). The optical reflectance as a function of incident angle was monitored and analyzed by fitting the experimental data to the well known Fresnel equation.

$$R = |r_{012}|^2 = \left| \frac{r_{01} + r_{12} \exp(2i\kappa_j d)}{1 + r_{01} r_{12} \exp(2i\kappa_j d)} \right|^2 \tag{1}$$

where

$$\kappa_j = \left[\varepsilon_j \left(\frac{2\pi}{\lambda} \right)^2 - \kappa^2 \right]^{1/2} \quad \text{and} \quad \kappa = \left(\frac{2\pi}{\lambda} \right)(\varepsilon_2)^{1/2} \sin\theta$$

The incidence angle, θ of light through the prism-metal interface determines the wave vector component κ which is parallel to the interface. λ is the wavelength of light in vacuum and ε_1 is the dielectric constant. The resonance angle can be determined at which the reflectance is a minimum in order to characterize the sensing behavior.
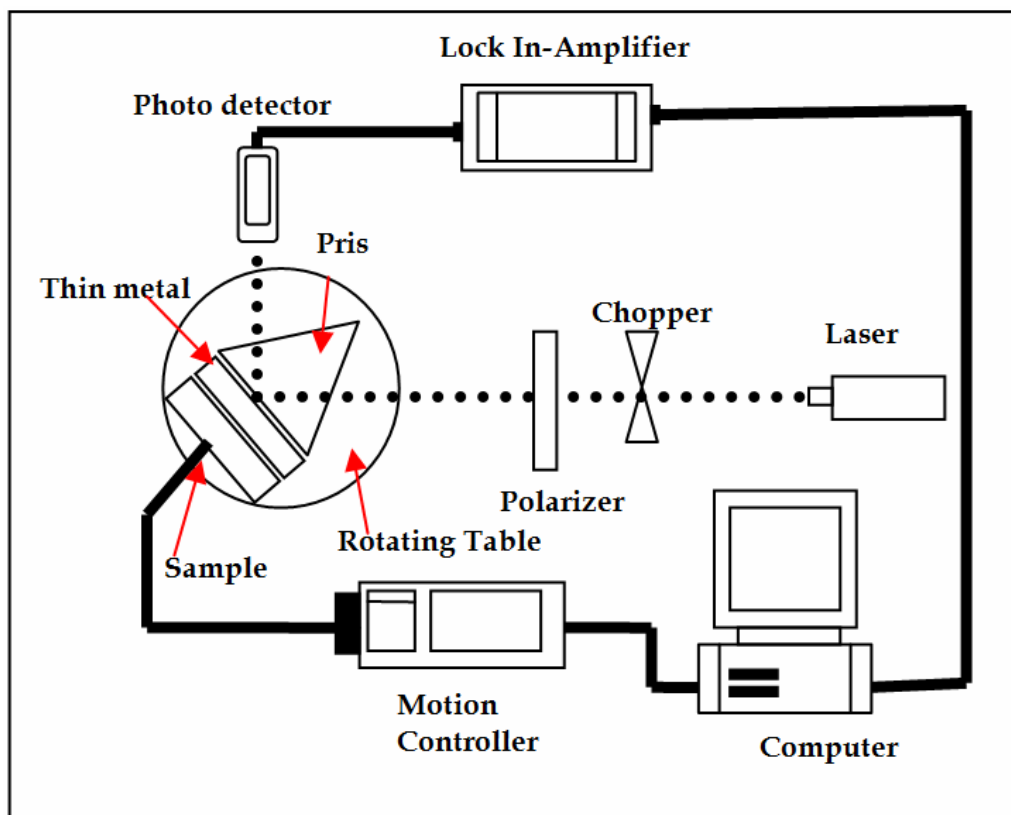
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Figure 1: Experimental setup for Surface Plasmon Resonance Technique

RESULTS AND DISCUSSION

In the surface plasmon resonance technique, the resonance angle is monitored which is very sensitive to the dielectric properties of the sample outside the gold surface. Therefore the immobilization of molecules on the gold surface or conformational changes in the immobilized molecules can be detected. It was observed that when the concentration of the medium outside the gold film was changed, the resonance angle gradually shifted to the right. The measurement was done immediately after the sample was injected into the sample holder.

Figure 2 shows the typical reflectance curve obtained for distilled water, methylene blue, rhodamine B and rhodamine 6G samples measured at a concentration of 0.006 mol/L. The resonance angle occurred at 60.64º, 61.15º, 61.46º and 62.45º for distilled water, rhodamine 6G, rhodamine B and Methylene Blue respectively. These shifts of the resonance angle were due to the difference in the dielectric constant of the samples.

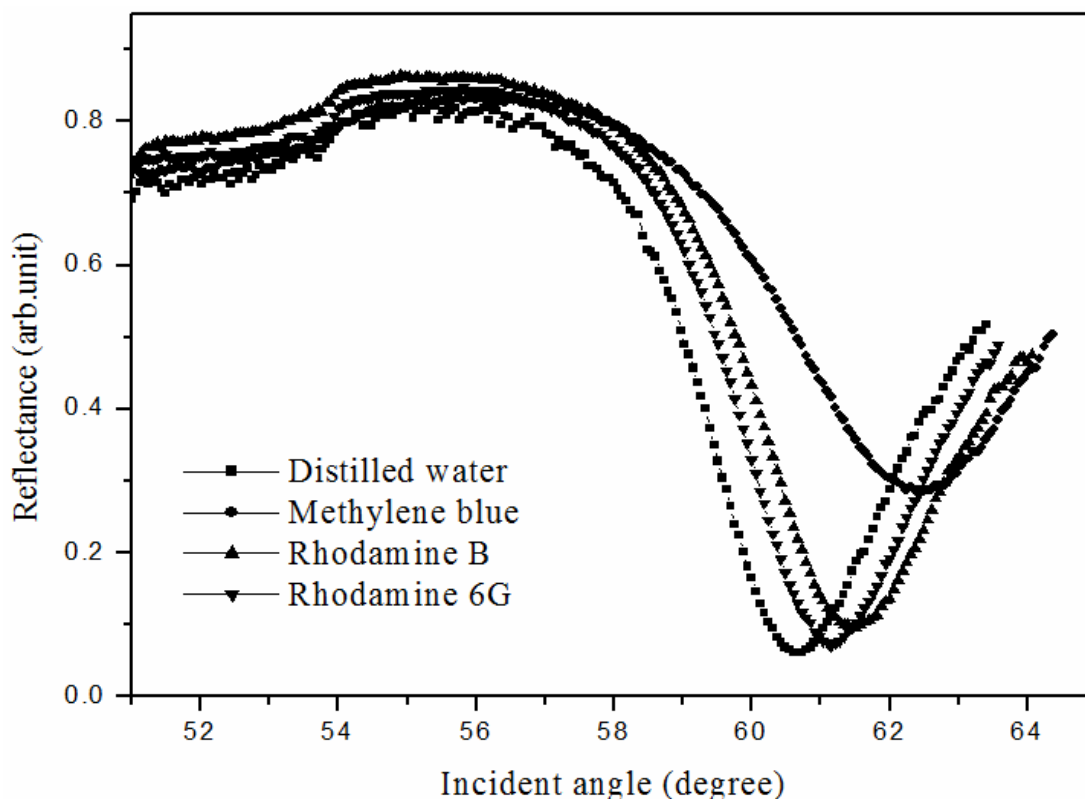Corresponding Author: nurulizrini@gmail.com

Figure 2: Reflectance curve for distilled water, rhodamine 6G, rhodamine B and methylene blue at a concentration of 0.006 mol/L.

Prior to the measurement, a preliminary test for distilled water was carried out where the refractive index of distilled water was obtained as 1.330 [4]. When the solution of different concentrations (%w/w) of dielectric sample was used, a shift in reflectivity was also observed. The correlation between the concentration of dye solution and the shift in resonance angle ($\Delta\theta$) is shown in Figure 3. The shift in resonance angle ($\Delta\theta$) shows a linear dependence with concentration.

The fitted results showed that the linear regression coefficient for methylene blue is 0.998, for rhodamine B is 0.997 and for rhodamine 6G is 0.996. Since the straight line pass through the origin, it is clear that lower concentrations of these samples can be measured using this method. The sensitivity of the detection for all three samples was recorded as 162.458º/(mol/L), 279.538º/(mol/L) and 452.763º/(mol/L) for rhodamine 6G, rhodamine B and methylene blue respectively.. The sensitivity of methylene blue in distilled water is higher than rhodamine B and Rhodamine 6G. Therefore the surface plasmon resonance angle was sensitive to methylene blue, followed by rhodamine B and rhodamine 6G.

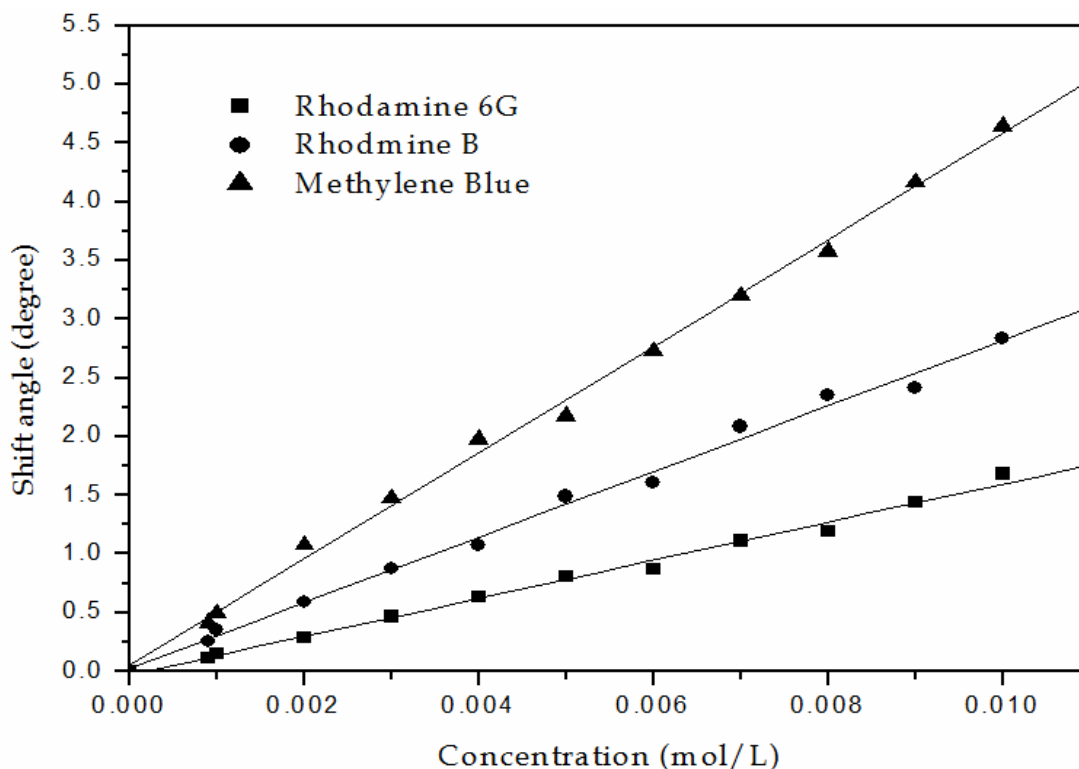Corresponding Author: nurulizrini@gmail.com

Figure 3: The shift of resonance angle versus rhodamine 6G, rhodamine B and methylene blue concentration (%w/w).

Since surface plasmon is sensitive to the change in the refractive index at a metal surface, detecting the chemical adsorption process at the surface was investigated by monitoring the real-time adsorption of dye solution on the gold surface. For this purpose, rhodamine B, rhodamine 6G and methylene blue solutions were prepared at three concentrations of 0.001, 0.005 and 0.010 mol/L. The reflectance change was accumulated from the time the solution was injected into the sample cell. By measuring $\Delta\theta_{spr}$, different behaviour was observed for the investigated samples. The adsorption kinetics for variable concentration of dye solution to gold layer was analyzed as shown in Figures 4(a-c). The trend are almost similar for all three samples but with different response time. At first, the shift of the resonance angle for rhodamine B was increased exponentially followed by an increase up to a definite value. These definite values were dependent on the initial concentrations of Rhodamine B in distilled water, although there were small differences in the shift of resonance angle among three different concentrations of rhodamine B in distilled water [5]. It is found that the resonance angle changes gradually with increasing concentration of rhodamine B in water. This result is related with the polarity of the solution [6].The same behaviour is observed for rhodamine 6G and methylene blue.

The solid lines in figure 3 correspond to the fitted theoretical expression [7].

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$$\Delta\theta(t) = \Delta\theta_{\infty}\left\{1 - \exp\left[-\frac{t}{\tau}\right]^{\beta}\right\} \qquad (2)$$

where $\Delta\theta_{\infty}$ is the saturation value which depends on the concentration of the solution, τ is the time constant and β represents a stretching coefficient.
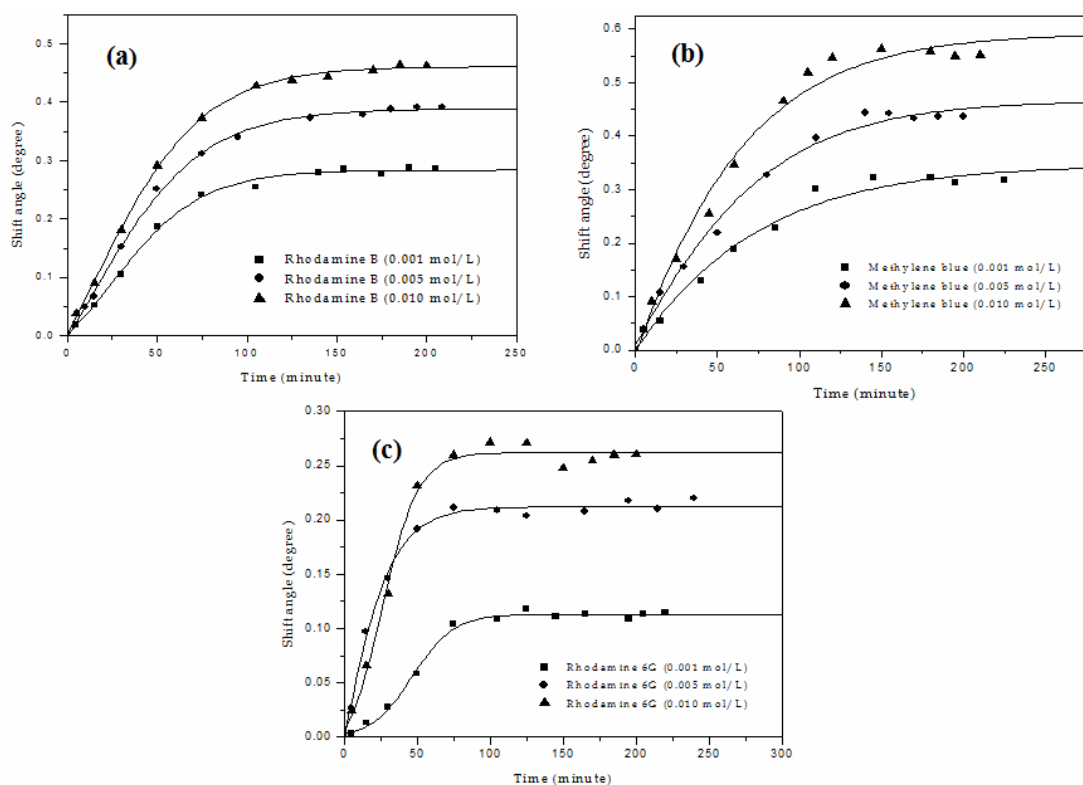

Figure 4: The shift of resonance angle versus time at different concentrations (%w/w) for sample (a) rhodamine B, (b) methylene blue and (c) rhodamine 6G

Using equation (2) the best fit for any dye concentration can be achieved and three parameters were retrieved. Figure 5 shows the stretching coefficient, β as a function of concentration for methylene blue, rhodamine B and rhodamine 6G. The exponent β always represents a distribution of potential barriers for relaxation process. In our case we observed $\beta > 1$, which would indicate a type of accelerated relaxation. It is a typical value for all the three dye molecules.
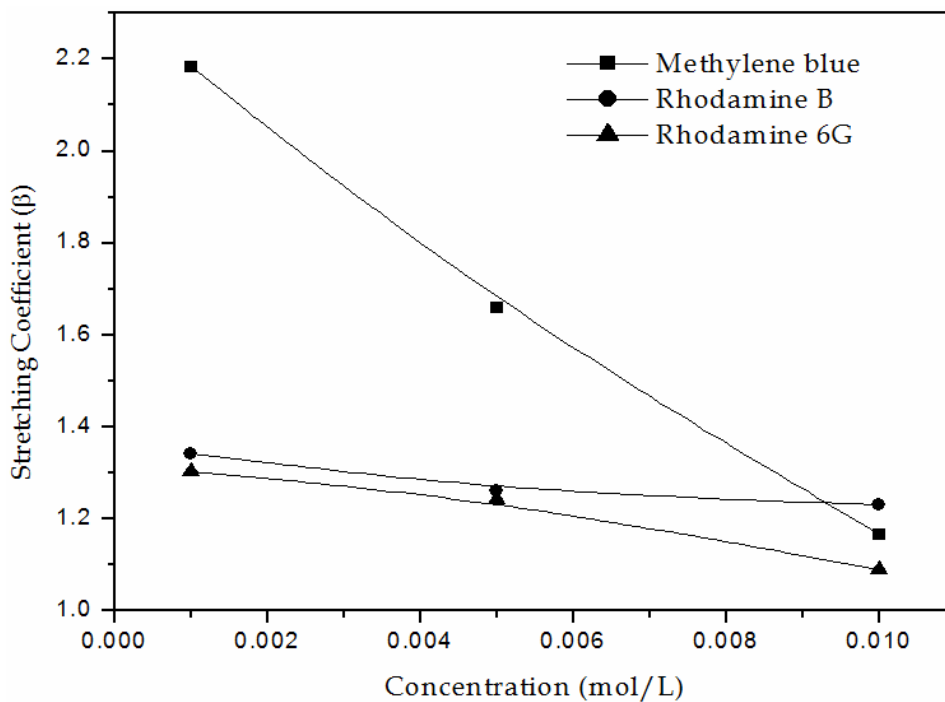
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Figure 5: Stretching Coefficient, β versus concentration for methylene blue, rhodamine B and rhodamine 6G
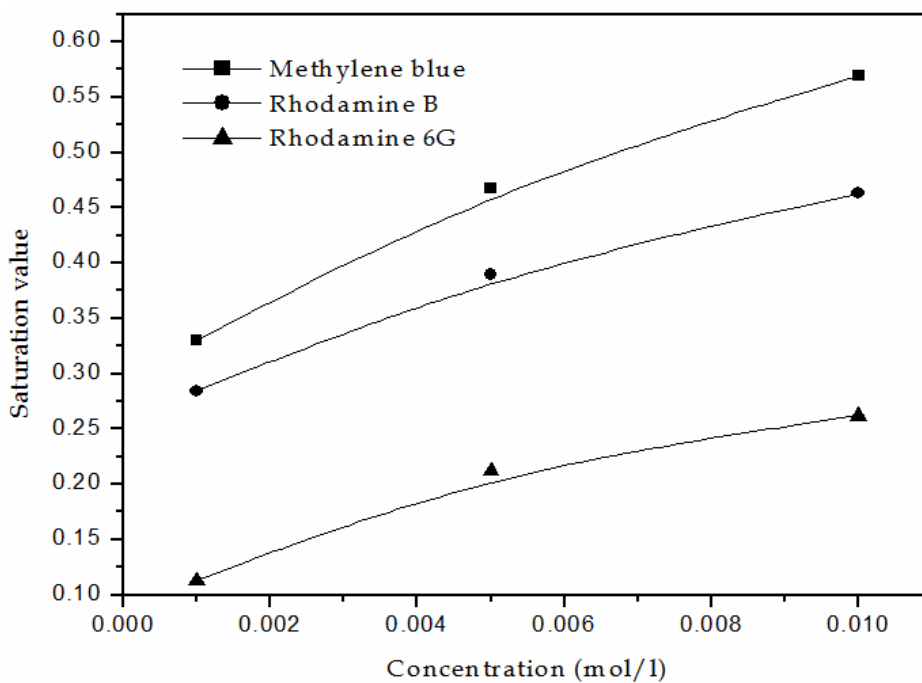

Figure 6: Saturation value, $\Delta\theta_\infty$ versus concentration for methylene blue, rhodamine B and rhodamine 6G.

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Figure 6 shows the saturated resonance angle, $\Delta\theta_\infty$ versus the concentration for methylene blue, rhodamine B and rhodamine 6G. For any type of investigated molecules, the calibration curves again show a linear dependence. We can see that the saturated resonance angle $\Delta\theta_\infty$ shows an increasing trend with sample concentration. This trend shows that the methylene blue has higher value of the saturated resonance angle, $\Delta\theta_\infty$ compare to the others. This may be explained by the fact that solutions with higher concentration have an increased density of solute molecules per unit solvent [8].
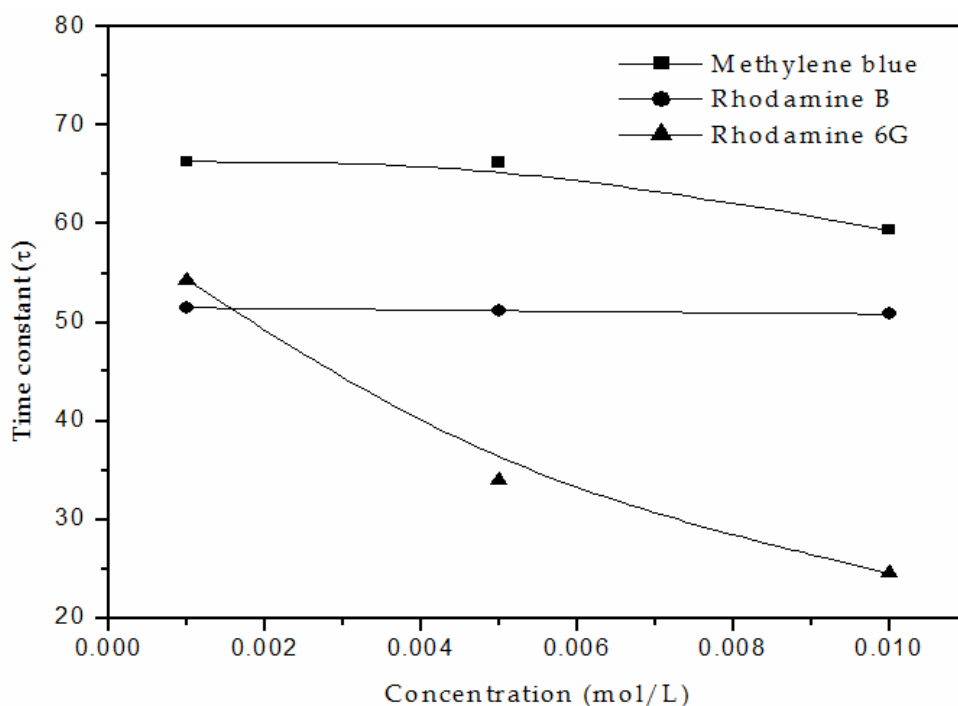

Figure 7: Time constant, τ versus concentration for methylene Blue, rhodamine B and rhodamine 6G.

The time constant τ strongly depends on the concentration as shown in Figure 7. It is noticeable that τ decrease as the concentration increase which is due to the order of magnitude in accordance with the group of dye. Increasing time constant may indicate either decreasing the number of accessible surface or a change in the chemical potential that influences the immobilization. Furthermore, the immobilization strongly depends on the shape and the molecular weight of the dye.

CONCLUSION

A simple optical sensor based on Kretschman surface plasmon has been tested for the detection of three dye solution (methylene blue, rhodamine B and rhodamine 6G). An arrangement for measuring the influence of concentration on the effective gold thin film

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is demonstrated. The kinetic behaviour of the system due to the self-assembling process on the gold surface for different types of dye has been described by using exponential fitting expressions for the $\Delta\theta(t)$ data.

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