Surface plasmon resonance measurement of polyethylene glycol in water

Nurul Izrini Ikhsan, W. Mahmood Mat Yunus, Zainal Abidin Talib and Zaidan Abdul Wahab
Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

(Received 26 December 2007)

The optical properties measurement of Au thin film towards Polyethylene Glycol (PEG) in water has been characterized using surface plasmon resonance (SPR) technique. SPR is a simple and direct optical technique for detecting some chemical entities. Surface plasmons can be excited by the attenuated-total-reflectance (ATR) method as proposed in the Kretschmann SPR technique. This method is very sensitive to the variations in the refractive index of the medium outside the metal thin film. When the medium outside the metal thin film (gold) is changed from air to PEG solutions, the resonance angle shifted with the increasing of the concentration. We observed that the shift of resonance angle $(\Delta\theta)$ increases linearly with the concentration of the sample. In the present work, we have chosen PEG 400, 4000, 10000, 20000 as a dielectric medium in Kretschmann configuration. The slope of the straight line shows the sensitivity of the detection and it was estimated to be 0.23º %w/w, 0.34º %w/w, 0.45º %w/w and 0.63º %w/w for PEG 400, PEG 4000, PEG 10000 and PEG 20000 in water. The sensitivity of measurement for PEG 20000 in water is higher than that obtained for PEG 10000, PEG 4000 and PEG 400.

I. INTRODUCTION

Polyethylene glycol (PEGs) is a family of water soluble linear polymers formed by the additional reaction of ethylene oxide (EO) with mono ethylene glycols (MEG) or diethylene glycol. The formula for polyethylene glycol is: $H(OCH_2\ CH_2\ )_n\ OH$ where n is the average number of repeating ethylene oxide groups. There are many grades of PEGs that represents them by their average molecular weight. For example, PEG 400 consists of a distribution of polymers of ranging molecular weight corresponds to an approximate average number of repeating EO groups (n) of ≈ 9. Polyethylene glycols are available in average molecular weight ranging from 200 to 20000. This wide range of products provides flexibility in choosing properties to meet the requirements of many different applications.

Surface plasmon resonance (SPR) is well known as a powerful and expensive optical method for the study of interface phenomena. SPR is an optical phenomenon arising in thin metal films under condition of total internal reflection which can produces a sharp dip in the intensity of the reflected light at a specific angle. This is called a resonance angle which depends on refractive index of the medium close to the non-illuminated side of the metal film. By keeping other factors constant, SPR is used to measure the change in the concentration of molecules in the surface layer of solution in contact with the sensor surface. SPR can be observed when an excitation source of energy (*p-polarized*) is directed towards a metal whose conduction band electrons can be approximated as free electron plasma. Under certain resonance conductions, collective resonating oscillation of free electrons may exist on the metal surface and produced a charge density wave propagating along the plasma surface. These charge fluctuations are known as surface plasmons (SPs). These SPs are accompanied by a mixed transversal and longitudinal electromagnetic field which has its maximum on the metal surface and decays exponentially away from the metal-dielectric interface [1].

The SPs can be excited by the so-called attenuated total reflectance (ATR) method proposed by Kretschmann [2]. Since the resonance angle is very sensitive to variations in the refractive index of the medium just outside the metal thin film, the technique has been found to be suitable for chemical and biomolecule characterizations [3-5]. In this paper, we used surface plasmon technique to measure the optical properties of polyethylene glycol in water.

Surface plasmon resonance is the result of optical excitation of a surface plasmon wave (SPW) along the interface between a highly conducive metal and a dielectric material. The conditions for excitation are determined by the permittivity of the metal and the sample material as well as the wavelength and angle of incidence of the light. The wave vector of the SPW (k_{sp}) can be approximated as [6].

$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_s}{\varepsilon_m + \varepsilon_s}} \qquad (1)$$

where ω is the radian frequency of the incident wave, c is the speed of light and $\varepsilon_{m,s}$ are the complex wavelength dependent permittivity of the sample (s) and metal (m). In order to excite an SPW, the x component of the incident wave vector (k_x) must match with k_{sp} such that

$$k_{sp} = k_x = \frac{\omega}{c}\sqrt{\varepsilon_p}\sin\theta \quad (2)$$

where ε_p is the permittivity of prism and θ is the angle of incidence. This condition can only be satisfied by TM polarized light and results in the incident light coupling to the SPW. Since $(\varepsilon_s = \varepsilon_r + i\varepsilon_i)$, the technique can be used to obtained ε_r and ε_i of the polyethylene glycol series. Therefore the present work aims to measure the optical properties for different series of polyethylene glycol in water.

III. MATERIAL AND METHODS

The surface plasmon resonance measurement has been carried out by measuring the reflected He-Ne laser beam (632.8 nm, 5 mW) as a function of incident angle. The optical setup consist of a He-Ne laser, an optical table driven by a stepper motor 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 the lock-in-amplifier (SR 530). The optical reflectance as a function of incident angle was obtained and analyzed for PEG 400, PEG 4000, PEG 10000 and PEG 20000 solutions. PEG 400 sample was prepared by dissolving certain weight of PEG 400 into distilled water to produce the solution concentration of 6.0 %w/w. Then 6.0 %w/w solution was diluted using dilution process to make final concentration of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 %w/w. Similar procedure was implied for preparing PEG 4000, PEG 10000 and PEG 20000 samples.

III. RESULTS AND DISCUSSION

Polyethylene glycol are polymers composed of repeating subunits of identical structure called monomers and are the most commercially important polyether. Poly (ethylene glycol) refers to an oligomer or polyethylene oxide. While PEG with different molecular weights find use in different applications and have different physical properties due to chain length effects and their chemical properties are nearly identical. This work explains the use of surface plasmon resonance technique to measure the optical properties of polyethylene glycol with different series of molecular weight.

Surface plasmon can be excited at the gold/air, and gold/polyethylene glycol series interfaces. The surface plasmon attenuated total reflection (ATR) spectra of gold/air, gold/polyethylene glycol solutions are presented in Fig. 1.

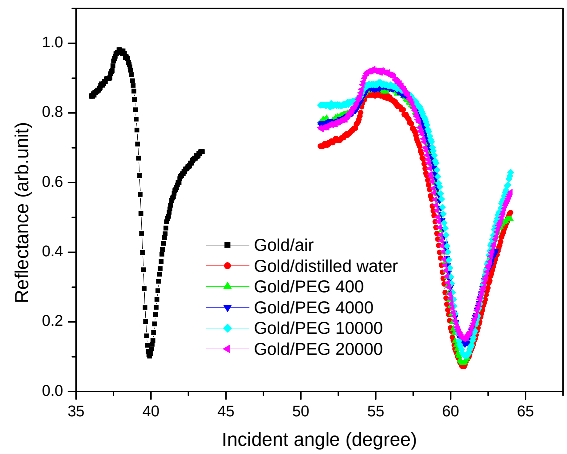

FIG. 1. Resonance curves for gold/air and gold/polyethylene glycol series.

Fig. 2 shows the reflectance curves measured for various concentrations of PEG series in distilled water. The resonance angle was observed at 60.79º for distilled water and 60.91º, 61.03º, 61.15º and 61.22º for PEG 400, PEG 4000, PEG 10000 and PEG 2000 at concentration of 3.5 %w/w. We observed that the reflectance curve for a gold/PEG series interface is broader than the curve for a gold/air interface as predicted from theoretical calculation [5]. The difference in resonance angle may due to the difference in dielectric constant between the sample and the values are corresponding to the amount of PEGs in distilled water.

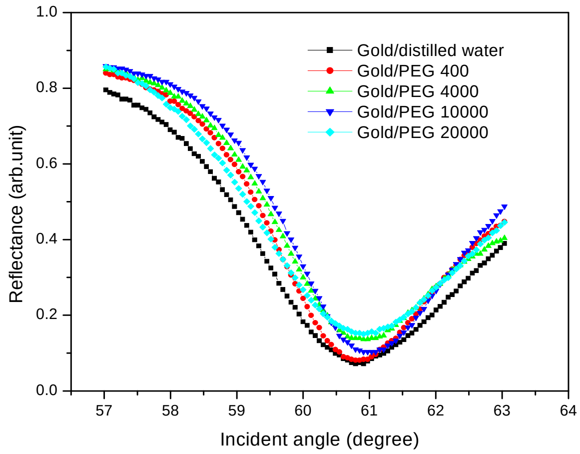

FIG. 2. Resonance angle for distilled water and polyethylene glycol series obtained at 3.5 %w/w.

By fitting the experimental data to the Fresnel equation [7,8], the values of real and imaginary part of dielectric constants ε_r and ε_i of four polyethylene glycol solutions were obtained. Figs. 3 and 4 show the values of real and imaginary part of dielectric constant, ε_r and ε_i. In the plot of ε_r value as a function of the PEG concentration, obviously they are linearly proportional to the concentration where ε_r for the sample increased with the increasing of solution concentration. Meanwhile, the graph for ε_i as a function of PEG concentration shows a non-linear graph but still increased with the increasing of solution concentration.

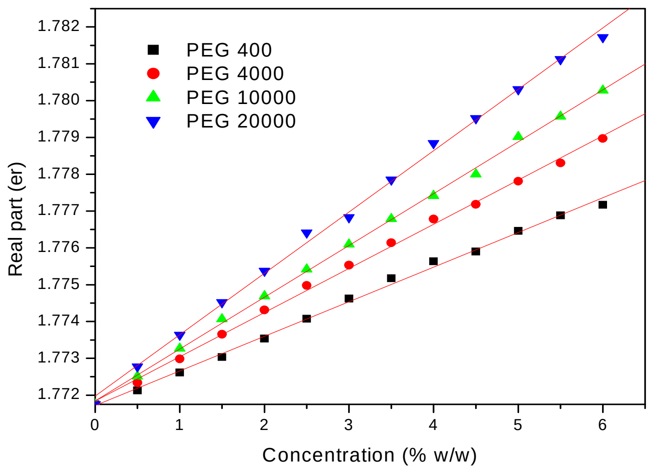

FIG. 3. Real part of dielectric constant, ε_r as a function of polyethylene glycol series concentration.

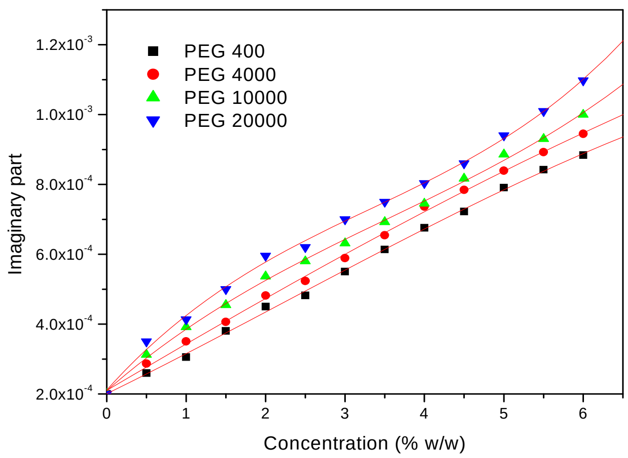

FIG. 4. Imaginary part of dielectric constant, ε_i as a function of polyethylene glycol series concentration.

The resonance angle is very sensitive to variations in the refractive index of the medium outside the metal film. When the different concentration of PEG series was attached, shifts of the reflectivity were obtained. The correlation between the PEG series concentration and the angular shift $(\Delta\theta)$ of resonance angle are shown in Fig. 5. The shift in resonance angle varies linearly with PEG series concentration. A linear relationship shows that the shift of resonance angle is directly proportional to the concentration of solution. The linear regression coefficients observed from the graph were 0.994, 0.997, 0.998 and 0.930 for PEG 400, PEG 4000, PEG 10000 and PEG 20000. The slopes of the straight line which gives the sensitivity of the sensor were obtained to be 0.23°/(%w/w), 0.34°/(%w/w), 0.45°/(%w/w) and 0.63°/(%w/w) for PEG 400, PEG 4000, PEG 10000 and PEG 20000. It shows that sensitivity of measurement for PEG 20000 in water is higher than that obtained for PEG 10000, PEG 4000 and PEG 400. This different may be due to the different in chemical structure of those four PEGs series solutions.

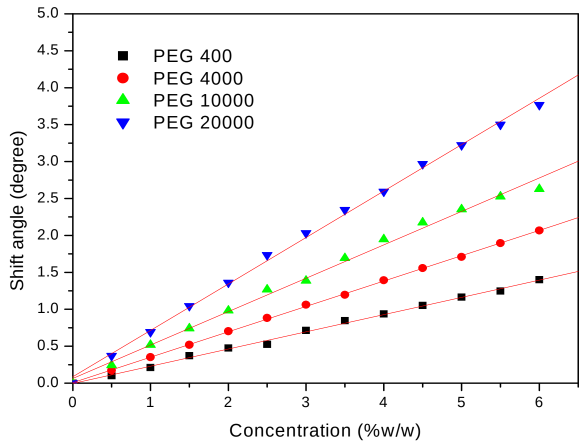

FIG. 5. SPR shift angle versus concentration for PEG 400, PEG 4000, PEG 10000 and PEG 20000 (%w/w).

IV. CONCLUSION

We have used SPR technique to measure the dielectric constant of polyethylene glycol series in water. The values of dielectric constant ε_r and ε_i as a function of concentration increase with the increasing of the amount of the solute in the solvent. The value of real part ε_r for all four samples is in range of 1.7669 to 1.835 while the imaginary part of dielectric constant ε_i is in the range of 0.0002 to 0.001. The shift of resonance angle $(\Delta\theta)$ increase linearly with the sample concentration in which the sensor sensitivity were found as 0.23°/(%w/w), 0.34°/(%w/w), 0.45°/(%w/w) and 0.63°/(%w/w) for PEG 400, PEG 4000, PEG 10000 and PEG 20000.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Department of Physics and SAGA for providing the research facilities and financial support. One of us (Nurul Izrini) would like to acknowledge the Ministry of Science Technology and Innovation (MOSTI) for the financial support through National Science Fellowship (NSF) program.

REFERENCES

[1] B. H. Ong, X. Yuan, S. C. Tjin, J. Zhang and H. M. Ng, Sensors and Actuators B, **114**, 1028-1034 (2006).

[2] E. Kretschmann, Z. Phys., **241**, 313-324 (1971).

[3] B. Liedberg, C. Nylander and I. Lundstrom, Sensors and Actuators, **4**, 299-304 (1986).

[4] X. Huang, M. T. Zhao, L. Janiszewska and P. N. Prasad, Surface Synth. Met., **24**, 245-253 (1988).

[5] S. Lofas and B. Johnsson, J. Chem. Soc., Chem. Commun., 1526-1528 (1990). doi:10.1039/C39900001526.

[6] C. Jung, *Surface Plasmon Resonance*, Masters Thesis, University of Washington (1991).

[7] G. T. Sincerbox and J. C. Gordon II, Appl. Opt., **20**, 1491-1494 (1981).

[8] L. Levesque, B. E. Paton and S. H. Payne, Appl. Opt., **33**, 8036-8040 (1994).