UNIVERSITI PUTRA MALAYSIA

OPTICAL PERMITTIVITY OF ALIPHATIC ALCOHOLS, POLYETHYLENE GLYCOLS AND DYE SOLUTIONS USING THE SURFACE PLASMON RESONANCE TECHNIQUE

NURUL IZRINI BINTI IKHSAN

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By

NURUL IZRINI BINTI IKHSAN

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

April 2009

Specially Dedicated to:

My beloved parents;
Ikhsan B. Sarpin & Esah Bt Ahmad
For their love, support and concern….

My dearest fiancé;
Amir Hafiz Izzudin B. Amir Sharifuddin
For his love, understanding, patience and care…

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For his encouragement, guidance and advice…

And all my friends…

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Chairman : Professor W. Mahmood Mat Yunus, PhD

Faculty : Science

Surface plasmon is a charge density wave that occurs at an interface between a thin metal film and dielectric medium. The most common means of excitation surface plasmon resonance is achieved through the Kretschmann configuration by utilizing the attenuated total reflection (ATR).

In this study, gold with purity 99.99% was deposited onto glass cover slip in a form of thin film (thickness ~ 50 nm) using sputtering technique which then coupled onto one surface of 60° prism using index matching oil. Liquid samples used as the dielectric medium were aliphatic alcohols; (methanol, ethanol and 1-propanol), polyethylene glycols (PEG) series; (PEG 400, PEG 4000, PEG 10000 and PEG 20000) and dye solutions; (methylene blue, rhodamine B and rhodamine 6G). The intensity of the optical

reflectivity was measured as a function of incident angle at the metal and dielectric interface.

The determination of the dielectric constant ε_r and ε_i for metal and liquid was carried out by fitting the experimental data to the theory using Fresnel Equation. It was found that the permittivity values of ε_r and ε_i for aliphatic alcohol, polyethylene glycols and dye solutions are linearly proportional to the concentration. The value of the real part of dielectric constant, ε_r is in the range of 1.767 to 1.811 while the imaginary part, ε_i is in the range of 2×10^{-4} to 6×10^{-2}.

In the case of resonance angle shift, the resonance angle increased with the increasing of the concentration. The shift in resonance angle ($\Delta\theta$) varies linearly with the concentration. Since the straight line passes through the origin, it is possible to use SPR technique for the detection of aliphatic alcohols, polyethylene glycols and dyes at very low concentration. The slopes of the straight lines represented the sensitivity of the detection. The large value of sensor sensitivity of 452.763°/(mol/L) is obtained for the methylene blue sample.

The kinetic behaviour of the system was also investigated by examining the self-assembling process on the metal surface in real time. The shift in resonance angle increased rapidly with time due to the immobilization of the molecules deposited on the gold thin film surface. For aliphatic alcohol solution at concentration of 0.100 mol/L, ethanol achieved a plateau region faster as compared to methanol and 1-propanol. For

PEG samples at a concentration of 5.5 %w/w, PEG 400 responded faster as compared to PEG 4000, PEG 10000 and PEG 20000 while for dye sample at concentration of 0.010 mol/L, rhodamine 6G responded faster as compared to both rhodamine B and methylene blue.

The experimental results of surface plasmon resonance show that the optical properties and the kinetic behaviour can be determined by using the surface plasmon resonance phenomenon. This works shows that this technique can be a good chemical optical sensor where is suitable to study molecule-dielectric interaction for aliphatic alcohols, polyethylene glycols series and dye solutions in water.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PERMITIVITI OPTIK TERHADAP LARUTAN ALKOHOL ALIFATIK , POLIETILENA GLIKOL DAN BAHAN PEWARNA MENGGUNAKAN TEKNIK RESONANS PLASMON PERMUKAAN

Oleh

NURUL IZRINI IKHSAN

April 2009

Pengerusi : Professor W. Mahmood Mat Yunus, PhD

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Plasmon permukaan ialah gelombang ketumpatan caj yang berlaku pada permukaan di antara filem tipis logam dan medium dielektrik. Cara yang paling biasa bagi meransang resonans plasmon permukaan boleh dicapai melalui konfigurasi Kretschmann dengan menggunakan pengecilan pantulan dalaman penuh (ATR)

Dalam kajian ini, emas dengan ketulenan 99.99% telah disaputkan di atas slip kaca dalam bentuk filem tipis (ketebalan ~50 nm) menggunakan teknik percikan, di mana kemudian dilekatkan kepada satu permukaan prisma 60° dengan menggunakan minyak indeks sepadan. Sampel cecair yang digunakan sebagai medium dielektrik ialah alkohol alifatik; (metanol, etanol dan 1-propanol), siri polietilena glikol (PEG); (PEG 400, PEG 4000, PEG 10000 dan PEG 20000) dan larutan bahan pewarna (metilin biru, rodamin B dan rodamin 6G. Eksperimen telah dilakukan dengan mengukur keamatan keterpantulan

optik sebagai satu fungsi kepada sudut tuju pada permukaan logam dan dielektrik. Penentuan pemalar dielektrik ε_r dan ε_i bagi logam dan cecair telah dilakukan dengan memadankan data eksperimen kepada teori menggunakan persamaan Fresnel. Didapati bahawa nilai permitiviti ε_r dan ε_i bagi larutan alkohol alifatik, polietilena glikol dan bahan pewarna adalah berkadar terus kepada kepekatan. Nilai bahagian nyata bagi pemalar dielektrik ε_r adalah di dalam julat 1.767 ke 1.811 manakala bagi bahagian khayal ε_i adalah di dalam julat 2×10^{-4} ke 6×10^{-2}.

Dalam kes anjakan sudut resonans, sudut resonans meningkat dengan pertambahan kepekatan. Anjakan sudut resonans ($\Delta\theta$) berubah secara linear dengan kepekatan. Oleh kerana garis lurus melalui asalan, teknik SPR ini boleh digunakan untuk mengesan alifatik alkohol, polietilena glikol dan bahan pewarna pada kepekatan yang sangat rendah. Kecerunan pada garis lurus mewakili kepekaan pengesanan. Kepekaan pengesan tertinggi adalah pada 452.76°/(mol/L) telah diperolehi pada sample metilin biru.

Perlakuan kinetik sistem juga telah diperiksa dengan memerhatikan proses berkumpul kendiri pada permukaan logam dalam masa nyata. Anjakan sudut resonans meningkat secara mendadak dengan masa yang mana berkaitan dengan endapan molekul pada permukaan filem tipis emas. Bagi larutan alkohol alifatik pada kepekatan 0.100 mol/L, etanol telah mencapai bahagian dataran tinggi lebih cepat berbanding dengan masing-masing metanol, dan 1-propanol. Bagi sampel-sampel PEG pada kepekatan 5.5 %w/w, PEG 400 bertindak balas lebih cepat berbanding PEG 4000, PEG 10000 dan PEG 20000 manakala untuk sampel bahan pewarna pada kepekatan 0.010 mol/L, rodamin 6G bertindak balas lebih cepat berbanding kedua-dua rodamin B dan metilin biru.

Keputusan eksperimen untuk resonans plasmon permukaan menunjukkan bahawa sifat-sifat optik dan perlakuan kinetik dapat ditentukan menggunakan fenomena plasmon permukaan. Teknik ini telah terbukti boleh dijadikan sebagai pengesan optik kimia yang berkesan yang sesuai untuk mengkaji tindak balas molekul-dielektrik pada larutan alkohol alifatik, polietilena glikol dan bahan pewarna di dalam air.

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I certify that a Thesis Examination Committee has met on 2 April 2009 to conduct the final examination of Nurul Izrini binti Ikhsan on her thesis entitled "Optical Permittivity of Aliphatic Alcohols, Polyethylene Glycols and Dye Solutions Using the Surface Plasmon Resonance Technique" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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Date: 21 May 2009

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 8 June 2009

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution

NURUL IZRINI IKHSAN

Date: 23/6/09

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FIGURE CAPTIONS

LIST 0F ABBREVIATIONS/NOTATION/GLOSSARY OF TERM

θ_I	Incidence angle
θ_{spr}	Surface Plasmon Resonance angle
$\Delta\theta$	The shift of resonance angle
$\Delta\theta_0$	The initial shift of resonance angle respect to distilled water
$\Delta\theta_\infty$	The saturated resonance angle
ε_r	Real part of dielectric constant
ε_i	Imaginary part of dielectric constant
ε_0	Dielectric constant of prism
ε_1	Dielectric constant of metal film
ε_2	Dielectric constant of dielectric
I	Wave field
μ	Magnetic permeability
n_p	Refractive index of prism
n_m	Refractive index of metal film
n_0	Refractive index of dielectric medium
k_x	Wavevector component along surface electromagnetic wave
k_{sp}	Wavevector of a plasmon
κ_1	Wavevector in media 1
κ_2	Wavevector in media 2
R	Reflection coefficient
$R_{\min}$	Reflectance minimum
I_0	Incidence light
I_r	Reflected light
λ	Wavelength
d	Thickness

c	Concentration
τ	Time constant
β	Stretching coefficient
ATR	Attenuated total reflection
Au	Gold
Ag	Silver
EO	Ethylene oxide
MEG	Mono ethylene glycol
MWR	Molecular weight relative
PEG	Polyethylene glycol
SPR	Surface plasmon resonance
SPW	Surface plasmon wave
SPs	Surface plasmons
QCM	Quartz Crystal Microbalance
M	Concentration solution
V	Volume of concentration
T	Temperature
Mol/L	Mol per liter
%w/w	Weight percent.

CHAPTER 1

INTRODUCTION

During the last two decades, we have remarkable research and development activity intended at the realization of optical sensors for the measurement of chemical and biological entities (Homola *et al.*, 1999). The first optical chemical sensors were based on the measurement of changes in absorption spectrum and were developed for the measurement of CO_2 and O_2 concentration (Brecht and Gauglitz, 1995). A large variety of optical methods have been used in chemical sensors and biosensors including ellipsometry, interferometer (white light interferometer), spectroscopy of guided modes in optical waveguide structures (grating coupler) and surface plasmon resonance. The chosen quantity is determined by measuring the refractive index, absorbance and fluorescence properties of analyte molecules or a chemo-optical transducing medium (Boisde and Harmer, 1996). The potential of surface plasmon resonance (SPR) for characterization of thin films (Pockrand *et al*., 1978) and monitoring processes at metal interfaces [Gordon and Ernst, 1980] was recognized in the late seventies. In 1982 the use of SPR for gas detection and biosensing was demonstrated by Nylander *et al.* (1982) and Liedberg *et al,* (1983 and 1995). Since then SPR sensing has been receiving continuously growing attention from scientific community. Development of SPR-sensing configurations as well as applications of SPR sensing devices for the measurement of physical, chemical and biological quantities has been described by Homola *et al.* (1999). In this area, SPR as a surface oriented method has shown a vast potential for affinity biosensors and allowing real-time analysis of bio-specific interactions without the use of labeled molecules.

1.1 Surface Plasmon Resonance (SPR)

SPR is an optical phenomenon occurs in thin metal film under condition of attenuated total reflection (ATR). This phenomenon generates a sharp dip in the intensity of the reflected light at a particular angle known as the resonant angle. This resonant angle depends on numerous factors including the refractive index of the medium (refractive index is directly interrelated to the concentration of dissolved material in the medium) close to the non-illuminated side of the thin metal film. By keeping other factors constant, SPR can be used to measure different concentration of molecules in the surface layer of solution in contact with the sensor surface (gold layer).

1.1.1 Attenuated Total Reflection

When a light beam hits a prism, the light bends towards the plane of interface and passing from denser prism to a less denser one. Varying the incidence angle (θ) will change the out coming light until a critical angle is achieved where all the incoming light is reflected within the prism. This is known as attenuated total reflection (ATR).

1.1.2 Surface Plasmons

In most surface plasmon resonance study, gold is used because it gives a SPR signal at suitable combinations of reflectance angle and wavelength. In addition, gold is chemically inert to solutions and solutes typically used in biochemical contexts (Biacore Ab, 1998). When the light is polarized with its electric field in the plane of incidence, the field causes collective oscillation of the electrons in the metal layer where the energy of the metal surface coincide with the incident photon and the charge density wave . The incident light is absorbed and the energy is transferred to the electrons which converted into surface plasmons. Photon and electron behaviour can only be described when they have either wave or particle properties. In agreement with the quantum theory, a plasmon is the particle name of the electron density waves. Therefore, in an ATR situation when the quantum energy of the photons is right, the photons are converted into plasmons and leaving a 'gap' in the reflected light intensity.

1.1.3 Momentum Resonance

Like all other variation, the photon to plasmon transformation must preserve both momentum and energy in the process. Plasmons have a characteristic momentum defined by factors that include the nature of the conducting film and the properties of the medium on either side of the film. Resonance occurs when the momentum of incoming light is equivalent to the momentum of the plasmons (resonance momentum). The momentum of the photons and plasmons can be described by a vector function with both magnitude and direction. The relative magnitude of the components changes when the angle or wavelength of the incident light changes. However, plasmons are restricted to the plane of the gold film and for SPR it is only the vector component parallel to the surface that matters. Therefore, the energy and the angle of incident light should be right (light is polarized with its electric field in the plane of incidence) to form surface plasmon resonance.

1.1.4 Evanescent Wave

In ATR, the reflected light generates an electric field on the opposite site of the interface. The plasmons create a comparable field that extends into the medium on either side of the film. This field is identified as the evanescent wave because the amplitude of the wave decreases exponentially with increasing distance from the interface surface and decaying over a distance of about one light wavelength (Nagata and Handa, 2000). The dept of the evanescent wave which is useful for measurements is within ~ 300 nm of the sensor surface. The wavelength of the evanescent field wave is the same as that of the incident light. The energy of the evanescent wave is dissipated by heat. The equations which describe how electric fields travel through a medium include a term for the properties of the medium and for light. This term is recognized as the refractive index. The light is seen as refracted because the photons have a different velocity in different media. In the same way, the velocity (and therefore the momentum) of the plasmons is changed when the composition of the medium changes. When the momentum change, the angle of incident light at which the resonance occurs was also changed and known as resonant angle or angular SPR (Markey, 1999) and (Akimoto, 2000). Alternatively, at a fixed angle of incident light, the wavelength can be varied until resonance occurs (Quinn, 2000). This is known as resonant wavelength SPR or spectral SPR and is not widely used (Akimoto, 2000). A full wavelength spectrophotometer can simultaneously observe the wavelength from 400 – 800 nm and is more accurate than angle measurements.