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Effect of metal ions on the absorption spectra and surface plasmon resonance of an azacrown indoaniline dye

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Abstract

The effects of the complexation of a metal ion with an azacrown indoaniline (**ACIA**) dye on absorption spectra were evaluated using the Pariser–Parr–Pople (PPP-MO) method. The **ACIA** dye carrying a monoazacrown moiety exhibited sensitivity to metal ion complexation using an optical sensor based on surface plasmon resonance (SPR). A multilayer sensing chip was prepared with the **ACIA** dye sensing layer coated on a gold layer. Using the **ACIA** dye as a metal ion sensing molecule, a highly selective response to Li^+ was observed. © 2001 Published by Elsevier Science Ltd.

Keywords: Pariser–Parr–Pople (PPP-MO); Surface plasmon resonance (SPR); Indoaniline dye; Azacrown; Ionophore; Metal ion sensor

1. Introduction

The coordination chemistry of lithium and other alkali metals was viewed until the 1960s as a rather barren area, made so since the singly charged and relatively large M^+ ions were held to have rather poor coordinating ability. The majority of known metal salt complexes were hydrates, although a few chelate complexes (e.g. with β-diketonate and salicylaldehyde ligands) were prepared by Sidgwick as long ago as 1925. Important developments began, however, with the Nobel prize-winning discovery by Pederson of the macrocyclic polyether or crown ether ligand [1,2], and continued with a second generation of related ligands such as the cryptnads [3,4] and the lariat ethers [5]. Such ligands wrap around the metal ion, encapsulating it to greater or lesser degree, and they are highly selective with regard to which metal cation can be accommodated. Lithium salts have been used in the treatment of manic depression and other neurological and psychiatric disorders [6]. In light of such applications, methodologies for the separation and determination of Li^+ are currently receiving much attention. Although ionophores for divalent cations and some alkali metal ions are well known [7,8], few carriers which are specific to Li^+ have thus far been described. The design of ionophores for Li^+ is difficult owing to the fact that lithium ions are smaller than both sodium and potassium ions but are strongly hydrated in aqueous solution [9] and, hence, few lithium ionophores

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have been synthesized. The sensitive and selective detection of metal ions is an ongoing research topic in biochemistry and analytical chemistry. Selective chromogenic reagents, both alone or in combination with a masking agent, have satisfactorily been used for the colorimetric determination of most of the commonly encountered metal ions. On account of its high sensitivity, surface plasmon resonance is becoming of increasing importance for chemical trace detection. The complex formation of ACIA with Li^+ and Na^+ has been investigated spectrophotometrically [10]. It was found that as the metal ion concentration increased, absorbance decreased and the colour changed from blue to pale purple (hypsochromic shift). In this paper, the effect of metal complex formation on the absorption spectral change was studied on the basis of PPP-MO results (i.e. HOMO-LUMO energy level and first excitation energies). Surface plasmon resonance (SPR) is one of the promising optical techniques for chemical sensing, and SPR configuration systems such as immunoassay [11], liquid [12], gas [13] and thin film [14] have been reported. A surface plasmon is a surface charge-density wave at a metal surface and it is well known that surface plasmons can be excited by the attenuated-total-reflectance (ATR) method reported by Kretschmann [15] (Fig. 1).

Since the resonance angle is very sensitive to variations in the refractive index of the medium just outside the metal thin film, the refractive index of a film (e.g. multilayer Langmuir–Blodgett film [16] or polymeric film [17]) can be obtained using the surface plasmon technique. The measurement of the refractive index of a bulk chemical sample can be used to determine the concentration of an analyte, assuming that the refractive index of a solution depends solely on analyte concentration. This can be performed by employing selective chemical sensing layers (e.g. selective membrane, chromoionophore, and specific binding layer). A chemical sensing layer consists of a thin film having optical properties that vary with concentration of the analyte to be used. We are currently working on the synthesis and study of newer derivatives of indoaniline dyes, which can potentially yield a new class of chromogens for the selective and quantitative detection of metal ions, both for biological and environmental applications. We have previously reported the synthesis, metal ion recognition [10] and X-ray crystallography [18] of an ACIA dye. In this paper we report the development of a Li^+ ion sensor and demonstrate that SPR is capable of sensing Li^+ ions using an ACIA dye.

2. Experimental

2.1. Preparation of sensor chip

A very thin cover glass ($n = 1.522$, $d = 0.13$ mm, Matsunami) with little difference of refractive index compared with a prism ($n = 1.515$, Sigma, BK7) was used as the substrate for a SPR sensor chip. A thin gold layer (500 Å thick) with high

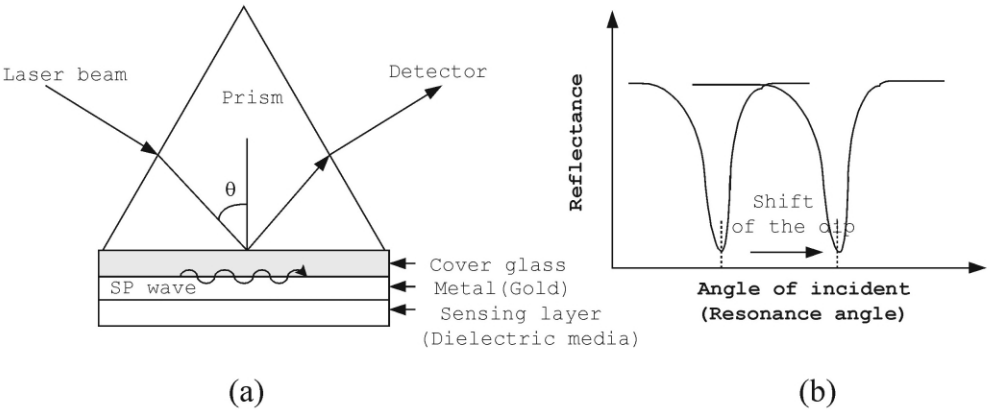


Fig. 1. (a) The Kretschmann configuration and (b) SPR-reflectance wave. The light reflectance is recorded as a function of the angle of incidence (θ).

chemical stability and a Ni–Cr under layer (30 Å thick) for adhesion on the above glass, was evaporated using a vacuum evaporation method.

The casting solution used to prepare the polymeric sensing film comprised a high M_r PVC–PVAc–PVA copolymer (Aldrich Chemical Company Inc., $M_r = 27{,}000$, 21.7 wt.%) DOP (dioctyl phthalate, Aldrich Chemical Company Inc., 37.7 wt.%) (as a plasticizer) liphophilic anionic site [potassium tetrakis(4-chlorophenylborate)] (Fluka, 29.0 wt.%) and indoaniline dye (11.6 wt.%) in THF (Junsei Chemical Co. Ltd.). Due to their higher stability and liphophilicity, borate salts were used for the cation selective membrane. This casting solution was spin-coated on the thin gold layer (membrane thickness = 0.4 μm) and the ensuing coated sensing membrane was dried at 75°C for 10 min. Optical contact between the prism and this sensor chip was achieved using a refractive index matching fluid ($n = 1.515$–1.517, Merck). Fig. 2 shows the construction of the sensing chip.

2.2. Experimental setup

This SPR system consisted of a laser diode (wavelength: 670 nm, output power: 5 mW, Melles Griot Co., Model; LDM145) for plasmon excitation, *p*-polarizer for inducing evanescent wave coupling with the plasmon, CCD (charged coupled device) array detector (Ureca Co., Model; CCD-20LH1-8) with 2048 pixels per inch for laser beam sensing after reflection from the SPR sensor units and a PC for analyzing data received from the CCD array detector. An optical jig for fixing the sensor chip and sample reserving cell on the θ-stage was used for observing the resonance angle of plasmon. Resonance angular shifts according to concentration of metal ions were detected as changes in the pixel output of the CCD array detector. The data received from the CCD array detector was transmitted to the PC after analogue/digital conversion using an 8-bit analogue/digital converter. As excitation of an surface plasmon wave (SPW) results in a drop in the intensity of the reflected light, this may be observed as a dip of the angular spectrum of the reflected light on the CCD array pixel output. Fig. 3 shows the setup of the SPR sensor system.

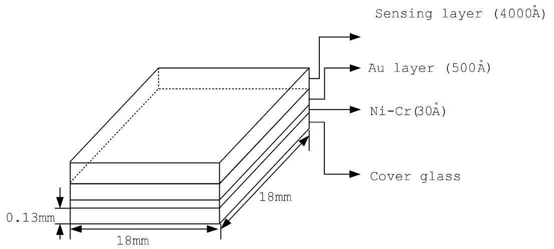


Fig. 2. Schematic of SPR sensing element.

2.3. Sample preparation

The concentration of metal ions [$M^{n+}(NO_3)_n$, $M^{n+} = Li^+, Na^+, K^+, Ca^{2+}$] ranged from 1×10^{-4} M to 1×10^{-11} M in 0.1 M Tris–HCl buffer (pH 7.4). One of the prepared standard samples were inserted some 0.5 ml into the cell on the sensor chip.

2.4. Measurements

Power intensity according to the change of the reflective angle by controlling θ-stage was detected by observing the refractive index shift achieved according to the change in metal ion concentration. Any shift in resonance angle resulted from a change in the dielectric constant according to the concentration of metal ions as the change in dielectric constant depends on the amount of metal ions complexed at the sensing membrane layer. The sensitivity and dynamic range of an integrated optic sensor designed for detecting metal ions depends

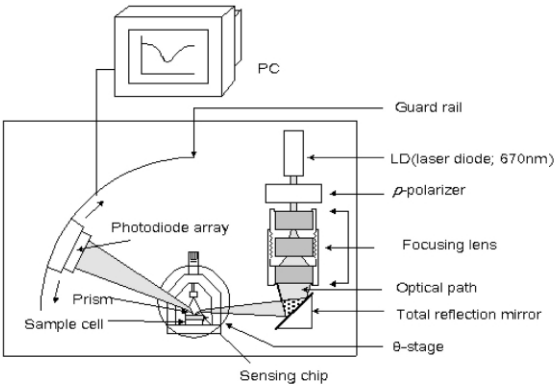


Fig. 3. Diagram of a SPR-based chemical sensor system.

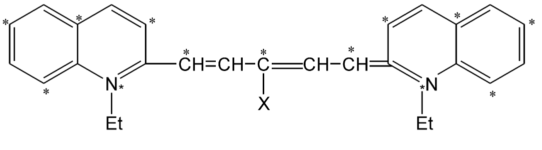
on the thicknesses of the thin film gold layer and the sensing membrane layer.

3. Results and discussion

If an ionophore bearing a chromophore or fluorophore in the vicinity of a metal ion binding site complexes a metal ion, the chromophore may be perturbed resulting in significant changes in both the absorption/emission spectra [19] and refractive index [20]. Chromoionophores are based on the idea that the selective complexation of a cation by a crown compound can be made visible by a colour effect initiated within the same molecule. This requires a chromophore adjacent to the ligand moiety and an electronic coupling between the two parts of the molecule. Complexation can induce either a wavelength shift in both absorption spectra and refractive index change.

3.1. Absorption spectral change

According to Dewar's rules, an electron withdrawing group attached at a starred position in dye **1** should give a hypsochromic shift [21]. This reasoning could be extended to the metal complex formation system of an ACIA dye because of the same odd alternant system.



X=H, λ_{max} : 708 nm
X=NO_2, λ_{max} : 580 nm

1

This finding can be interpreted by focusing attention on the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular molecular orbital (LUMO) by means of the PPP-MO method. The absorption spectra caused by the π–π* transition can be calculated by the PPP-MO method [22].

PI SYSTEM for windows is a commercial program based on a modified PPP SCF–CI–MO method for rapid and convenient calculations. All bonding and nonbonding interactions between the π atoms are calculated by means of Roothaan's formula for *p–p* overlap integrals. The calculation of the configuration interaction occurs from the ground state for the lowest 36 singly excited states. A small weakness is that there is no facility to edit the library of parameters.

Fig. 4 shows the spectral changes that were induced by adding Li^+ to ACIA dye in CH_2Cl_2–CH_3CN (4:1/v:v); as the Li^+ concentration increased, absorbance decreased and the colour changed from blue to pale purple (hypsochromic shift). The chromogenic reagents consists of a donor and acceptor component, which results in the presence of a charge transfer band in the absorption spectra. Interaction with the metal ion could have destabilized the donor part (macrocyclic nitrogen atom) of the dye molecule, leading to a hypsochromic shift of the charge transfer band. The interaction with metal cations affects the lone

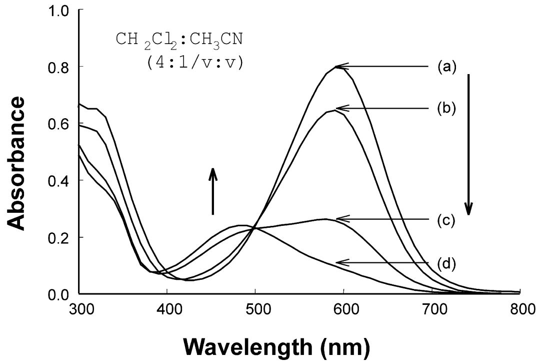


Fig. 4. Effect of Li^+ concentration on the absorption of spectra of ACIA dye (5×10^{-5} M): [Li^+] (a) 0, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 5×10^{-2} M.

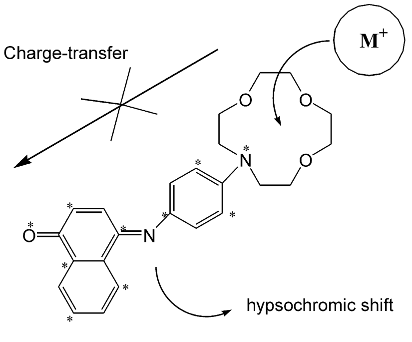


Fig. 5. The effect of complex formation on a absorption spectra.

pair of electrons of the macrocyclic nitrogen atom, thus inhibiting its donor ability. As a result, a hypsochromic shift of $\lambda_{\max}$ was observed, combined with a hypochromic effect (Fig. 5).

The effect of complex formation between metal ions and the donor azacrown moiety of the ACIA on energy levels of the HOMO and the LUMO were calculated, and the results are shown in Fig. 6. Complex formation can be evaluated by increasing the valence state ionization potential level of the macrocyclic nitrogen atom.

From the results shown in Fig. 6, the following observations were made. Variation of the valence state ionization (VSIP) factor of the macrocyclic nitrogen atom had a greater effect on the energy level of HOMO than LUMO, and an increase in the VSIP factor (i.e. simulating a weaker donor) produced a hypsochromic band shift. The correction factor for the electronegativity was used to determine the degree of hybridization as well as simulate variable substituents on a π system. The magnitude of the correction factor is proportional to the VSIP of the atom.

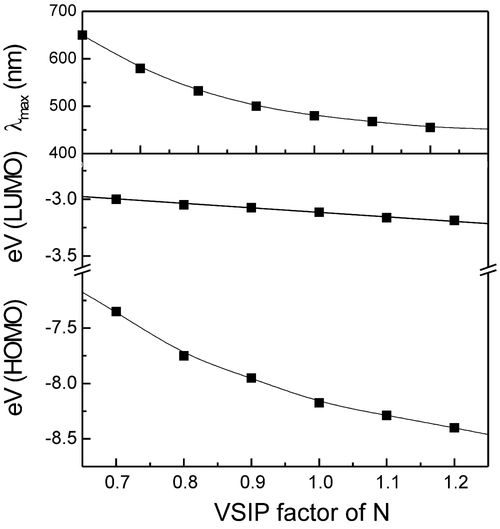


Fig. 6. Effect of metal complexation on energy levels of HOMO/LUMO and $\lambda_{\max}$ of ACIA.

3.2. SPR study

The development of sensors which provide an optical transduction of the chemical recognition process has become a highly relevant and rapidly expending area in analytical chemistry [23]. In this context, the design of fluorescent or chromogenic chemosensors for the selective detection of low concentrations of ions is an active research area. SPR has become increasingly popular as a tool for the qualitative and quantitative sensing of interactions between biochemicals. SPR is observed as a sharp dip in the dependence of the intensity of *p*-polarized light reflected from a metal film. In the most frequently used SPR biosensors, binding of the reactants are recorded as a shift of the angular position of the reflected intensity minimum. Highly selective ion sensing SPR systems for the determination of metal ions have been prepared using plasticized PVC–PVAc–PVA membranes containing dithiosquarylium dye [24]. The results indicated that DTSQ showed a striking selectively for Ag^+ complexation. In the surface plasmon method, the resonance angle is very sensitive to variation in the refractive index of the medium outside the metal film (Fig. 7).

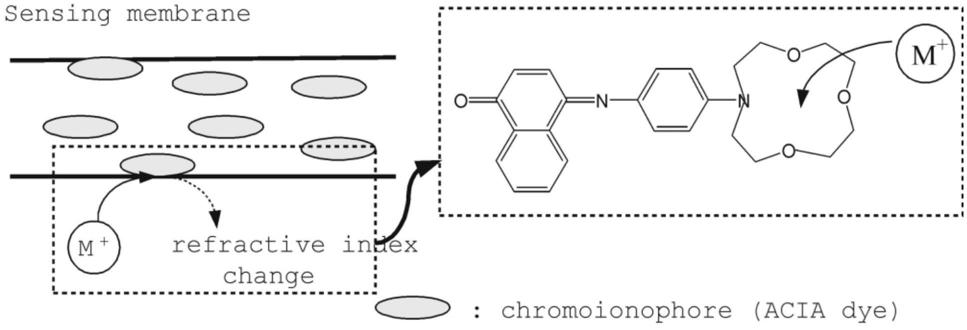


Fig. 7. Schematic representation of the refractive index change in sensing membrane.

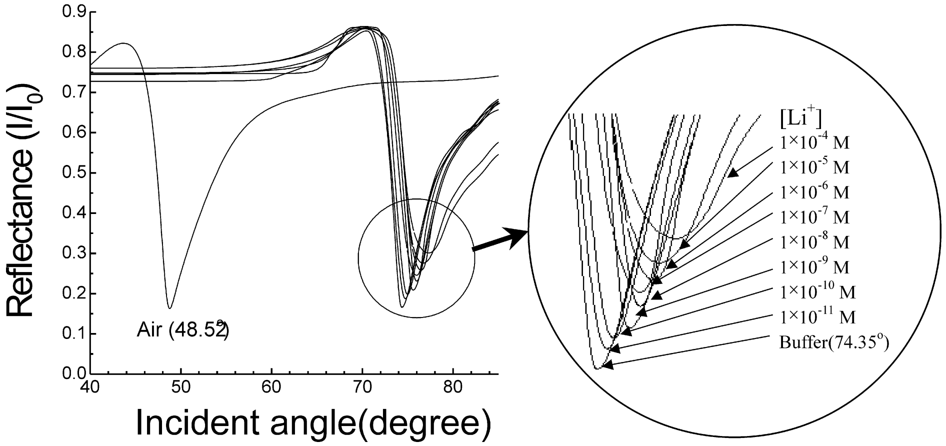


Fig. 8. The effects of coating a gold film with sensing membrane containing ACIA dye on SPR waves.

When the medium outside the sensing membrane of the ACIA dye was changed from air to a buffer solution, the resonance angle changed from 48.52 to 74.35° (Fig. 8). Fig. 8 shows the SPR waves for gold coated with a film of ACIA dye as a function of Li$^+$ concentration; as the Li$^+$ concentration increased, the resonance angle also increased. Fig. 9 shows that the addition of other metal ions such as K$^+$, Ca^{2+}, Na$^+$ up to 1×10^{-4} M did not have any significant effect on the shift in the resonance angle.

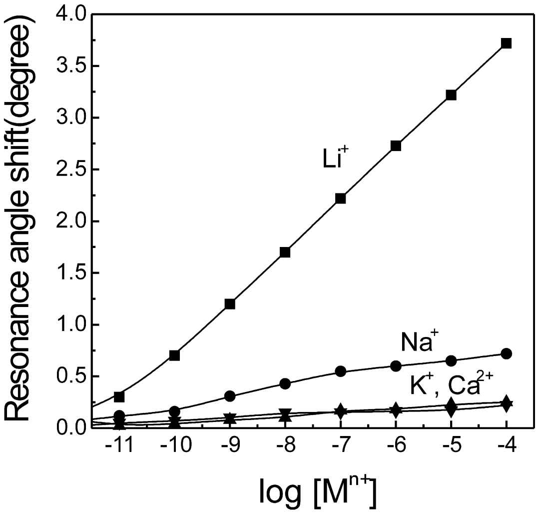


Fig. 9. Calibration plots for metal ions obtained with SPR.

Owing to the trace detection and specific resonance to Li$^+$ in SPR, the ACIA dye appear to the potentially suitable for practical SPR sensor application.

Acknowledgements

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