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Optical Absorbency Study on the Hydration of Polyvinylpyrrolidone Films Containing Cobalt Chloride

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Polymer films are used as sensing membranes of sensors for various chemical species in gas and liquid. Recently sensing devices using an optical fiber have drawn considerable attention because of advantages over electrochemical ones.^{1,2} Cobalt (II) chloride (CoCl_2) entrapped in polymer films has been studied for optical moisture detection by many workers.³⁻⁷ In spite of these reports, fundamental knowledge on spectroscopic and water sorptive properties is insufficient.

The work described here is part of an ongoing investigation into the possible applications of optical methods for quantitative moisture sensor system. In a previous study,⁸ we examined the relative humidity (*RH*) dependence of the absorption spectrum and water vapor sorption of polyvinylpyrrolidone (PVP) films containing CoCl_2 . It was concluded that, when *RH* increases, the 4-coordinate form of a cobalt ion changes to the 6-coordinate one and the amide group of the polymer coordinating to the cobalt ion is replaced by a water molecule. In the above study, however, the result is qualitative due to a single beam system used in the measurement of absorption spectrum. In this report, the relation between the absorbance of films and ambient humidity was investigated quantitatively.

Changes in absorption spectrum of the PVP films with *RH* were compared with the absorption spectra of *N*-methyl-2-pyrrolidone solutions of CoCl_2 , which were measured at various water concentrations. The absorbance-*RH* curves of the film are discussed in relation to the coordinate state of CoCl_2 in the polymer.

EXPERIMENTAL

Sample Preparation

Polyvinylpyrrolidone (PVP) (MW 360000, Nacalai Tesque), *N*-methyl-2-pyrrolidone (MP) (guaranteed reagent, Ishizu Pharmaceutical), and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (guaranteed reagent, Kishida Chemical) were used as received. Aqueous solutions were prepared with 3.8% (g/100 ml solution) of PVP and various concentrations of CoCl_2 at 0, 0.167, 0.333, and 0.667% (g/100 ml solution). 0.2 ml of each solution was cast on a 36×13 mm glass plate to produce moisture sensitive films containing CoCl_2 at various concentrations of 0, 0.33, 0.67, and 1.35 mol kg^{-1} (mol kg^{-1} PVP), respectively. Film thickness was about $16 \mu\text{m}$, as calculated from the volume of the coated solution by assuming that the density of all films is equal to 1.0.

Anhydrous CoCl_2 was prepared by drying $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 160°C under vacuum and dissolved in MP at concentrations of 0, 0.33, 0.67, and 1.35 mol kg^{-1} (mol kg^{-1} MP).

Measurement of the Absorption Spectra of PVP Films

A gas flow system was constructed by use of a Shin-ei SRH-1R humidity generator. The absorption spectrum of the sample was measured using a JASCO UVDEC-1 spectrometer under the condition of desired relative humidity (RH). The measurements were carried out at $20.0 \pm 0.2^\circ\text{C}$. Detail procedures can be found in the preceding paper.⁹

Measurement of the Absorption Spectrum for MP Solutions

The water concentration in the PVP film was determined previously⁸ when the film was equilibrated in air streams of various RH s. To a measured volume of the MP solution of CoCl_2 was added water so that the water concentration became the same as that in the PVP film. For example, water concentrations used for the MP solution containing 1.35 mol kg^{-1} of CoCl_2 were 66.7, 41.2, 16.3, 11.1, 6.2, and 0 mol kg^{-1} (mol kg^{-1} MP), which are the same as the water concentrations in the PVP film at 91, 81, 62, 42, 22, and 0% RH , respectively, in the desiccation process. The absorption spectrum of the MP solutions was measured using a Shimadzu UV-2100S spectrometer and a remountable flow-through cell with a path length of $25 \mu\text{m}$.

RESULTS AND DISCUSSION

Humidity Dependence of Absorption Spectrum

Absorption spectra of a PVP film containing 1.35 mol kg^{-1} of CoCl_2 were measured starting at 0% RH and ending at 90% RH . The results are shown in the range from 450 to 750 nm in Figure 1. Overall decrease in absorbance is observed in the range from about 550 to 720 nm with increasing RH . In addition, it can be seen

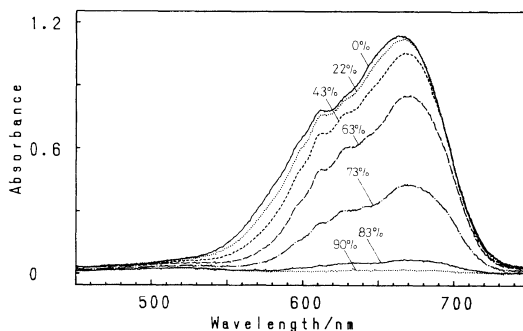


Figure 1. Absorption spectra of a PVP film containing 1.35 mol kg^{-1} CoCl_2 at a varying RH .

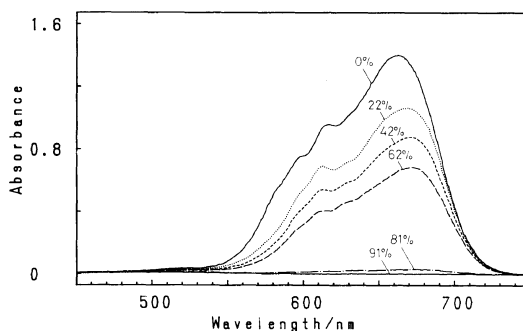


Figure 2. Absorption spectra of an MP solution containing 1.35 mol kg^{-1} CoCl_2 at varying RH s, which correspond to the water concentration used in the measurement.

that the absorption maximum shifts from 666 nm at 0% RH to 673 nm at 71% RH . Similar spectral features were also observed for both PVP films containing 0.33 and 0.67 mol kg^{-1} of CoCl_2 .

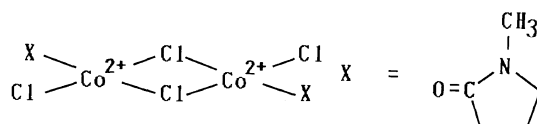
Changes in absorption spectrum of the PVP film with RH were compared with the absorption spectra of MP solutions of CoCl_2 mixed with a varying amount of water. The spectral change for the MP solution of 1.35 mol kg^{-1} CoCl_2 is shown in Figure 2. The absorbance decreases as a whole in the range from about 550 to 720 nm with increasing water concentration from 0 to 66.7 mol kg^{-1} , which corresponds to the increase of RH from 0 to 91%. This is apparently the result of alteration of cobalt (Co) complexes from the 4-coordinate to the 6-coordinate. It has been

demonstrated that MP¹⁰ and PVP¹¹ form complexes with transition metal ions such as Co²⁺ in which the metal atom is coordinatively bonded to the carbonyl oxygen atom of the pyrrolidone residue. Therefore, it is expected that this type of coordination bond exists herein in MP solutions and PVP films and participates in the change of Co complexes from the 4-coordinate to the 6-coordinate.

A longer-wavelength shift of the absorption maximum of about 665 nm is also observed in analogy with the absorption spectrum of PVP films. The absorption maximum shifts from 661.6 to 671 nm for the MP solution of 1.35 mol kg⁻¹ of CoCl₂ when the water concentration is increased from 0 to 16.3 mol kg⁻¹, which corresponds to an *RH* change from 0 to 62% for the PVP film. Shifts of the absorption maximum were 660.3→671 nm and 660.8→671 nm, respectively, for the MP solutions of 0.33 and 0.67 mol kg⁻¹ of CoCl₂ when the same increase of the water concentration was achieved. It seems that these shifts of the absorption maximum are the result of change in relative intensity of two different maxima; the absorption maximum of about 665 nm is supposed to consist of the two maxima located at about 660 and 670 nm. These maxima may be attributed to CoX₂Cl₂ and CoXCl₃⁻, respectively, where X is the carbonyl group of MP. It has been demonstrated that the addition of water to an acetone solution of CoCl₂ makes the absorption spectrum resemble that of CoCl₃⁻.¹² A similar effect of addition of water is expected to occur in MP solutions. It seems that water molecules knock chloride ions away from a Co complex; the chloride ion attacks another complex and eliminates a carbonyl group of MP, generating CoXCl₃⁻.

In addition, the absorption maxima at the water concentration of 0 mol kg⁻¹ are 660.3, 660.8, and 661.6 nm, respectively, for MP solutions of 0.33, 0.67, and 1.35 mol kg⁻¹ of CoCl₂. Thus, when a higher concentration of CoCl₂ is used, this maximum becomes longer,

indicating an increase in relative intensity of the maximum of about 670 nm. It seems that a higher concentration of CoCl₂ produces binuclear complexes held together by chloride ions, which have the structure



Although the concentration of CoCl₂, 1.35 mol kg⁻¹, is smaller than the corresponding concentration of MP in the solution, 10.1 mol kg⁻¹, this concentration seems sufficient to form binuclear complexes. Since each Co ion of the binuclear complexes forms three bonds to chlorine atoms in a similar manner to CoXCl₃⁻, these complexes are considered to have an absorption maximum at the same wavelength as CoXCl₃⁻. Therefore, the relative intensity of the maximum at about 670 nm is larger at a higher concentration of CoCl₂, where more binuclear complexes exist in the solution. Little difference in the shift of the absorption maximum was observed between PVP films containing different concentrations of CoCl₂, but a small amount of binuclear complexes is probably formed also in dry films.

Absorbance vs. *RH* Curve

The *RH* dependence of the absorbance at 670 nm of the PVP-CoCl₂ films is shown in Figure 3. The absorbance decreases slowly with increasing *RH* in the range from 0 to 63% *RH* and drops steeply in the range from 63 to 83% *RH*. Figure 4 shows the absorbance at 670 nm of the MP solutions as a function of *RH* corresponding to the water concentration used in the measurement. These curves of absorbance vs. *RH* for the MP solutions should be compared with those in the desiccation for PVP films, depicted in Figure 3, because the water concentrations of the MP solutions were determined to be the same as those in the desiccation of the PVP film. It is found by this

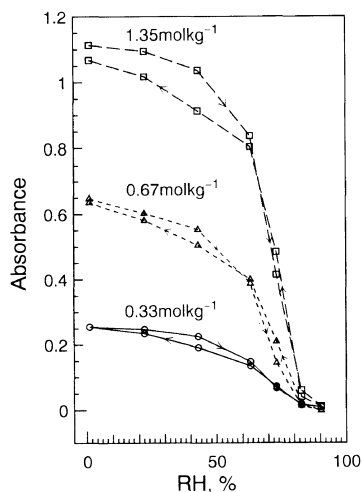


Figure 3. Absorbance at 670 nm vs. *RH* curves for PVP films containing various concentrations of CoCl_2 .

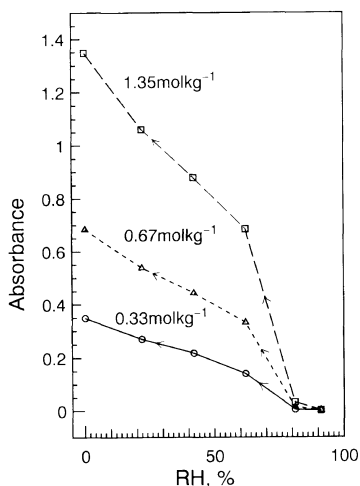


Figure 4. Absorbance at 670 nm vs. *RH* curves for MP solutions containing various concentrations of CoCl_2 . *RH* corresponds to the water concentration used in the measurement.

comparison that the absorbance less steeply decreases with increasing *RH* in the low- and middle-*RH* regions for the PVP films than the case of MP solutions. This indicates that Co complexes in the film interact with water less easily than those in solution at the same concentration of water. It seems that the water molecules adsorbed in the film in the low- and

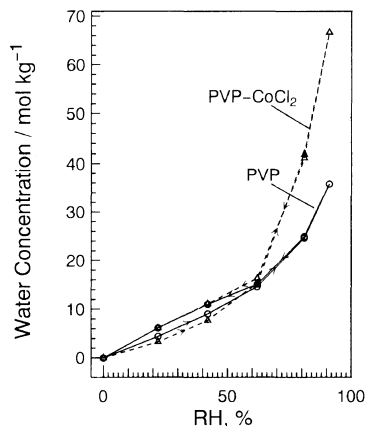


Figure 5. Water concentration in PVP films with and without CoCl_2 (1.35 mol kg^{-1}) at varying *RH*, which was changed from 0% to 91% and back to 0%.

middle-*RH* regions are attracted mainly by the amide groups of PVP and are less coordinated to the Co ion.

This idea is supported by the water-vapor sorption isotherm. Figure 5, obtained by replotting the data in the previous report,⁸ shows the humidity dependence of the water concentration (mol kg^{-1} or mol kg^{-1} PVP) in PVP films with and without CoCl_2 (1.35 mol kg^{-1}). The water concentration of the film containing 1.35 mol kg^{-1} of CoCl_2 is almost the same below 62% *RH*, but is much higher above 62% *RH* than that of the original PVP film. It has been reported that an ethylene-vinyl alcohol copolymer containing sodium chloride sorbs water vapor more and faster than the copolymer without salt.¹³ In contrast, the water-vapor sorption of the PVP film is enhanced by CoCl_2 only at higher *RH*s than 62% *RH*. The ability of CoCl_2 to make the film hygroscopic is depressed in the low- and middle-*RH* range, because Co complexes are shielded by polymer chains and can not easily interact with the adsorbed water.

Hysteresis appears to some extent in the curves of absorbance vs. *RH* for the PVP films in Figure 3. The curves in the desiccation are slightly lower below 63% *RH* but slightly higher above 63% *RH* than the curves in the

ion against the CoX_2Cl_2 complex, which results in the red shift of the absorption maximum. The formation of CoXCl_3^- is conceivable because this ionic entity may be more stable in a polar medium than a neutral one, CoX_2Cl_2 ; the polarity of the film is gradually increased by adsorbed water. The participation of CoXCl_3^- was proposed also in the hydration of gelatin films containing CoCl_2 .⁹ In fully hydrated films (c), most complexes are still linked to at least one carbonyl group, as concluded previously.⁸ The basis for this conclusion is the observation in the IR spectrum of a PVP film containing CoCl_2 . The amide I band is split into two peaks at 1678 and 1636cm^{-1} in the dry film due to coordination of some carbonyl groups. The two peaks are put together to produce a broad peak at 1655cm^{-1} when the film is hydrated, indicating that many carbonyl groups are coordinated to the complex.

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