SHIMADZU
Excellence in Science

UV-Vis Spectrophotometers UV-1900i/UV-2600i/UV-3600i Plus

Application News

Evaluating Chromotropism with a Spectrophotometer: Solvatochromism and Thermochromism

Kazuki Sobue

User Benefits

- Observe changes in absorbance while varying sample temperatures.
- The TCC-100, a thermoelectrically temperature-controlled cell holder controls sample temperatures in the range of 7 to 60 °C without the need for cooling water.
- The CPS-100, a six-cell thermoelectrically temperature-controlled cell positioner controls the temperatures of up to six samples concurrently.

■ Introduction

Reversible changes in optical properties due to external stimuli are referred to collectively as chromotropism. For example, the changing of a color from exposure to light is called photochromism, from heat is called thermochromism, and from a change in solvent polarity is called solvatochromism. These chromotropic phenomena have everyday applications, such as checking moisture absorption with silica gel and the printing of receipts. While UV-Vis spectrophotometers are used to measure these phenomena quantitatively, they require additional equipment depending on the type of external stimulus causing the color change. So while, solvatochromism can be measured without additional equipment, measuring thermochromism requires a device to heat the sample. (Application News 01-00016 describes using a UV-Vis spectrophotometer to measure thermochromism in a solid sample.) Measuring photochromism requires irradiating the sample with light, which can be performed using Shimadzu's dedicated photoreaction evaluation system called Lightway. More detailed information about Lightway can be found in Application News No. A625.

This Application News describes an evaluation of the solvatochromism and thermochromism of a metal complex solution. To measure the thermochromism, a thermoelectrically temperature-controlled cell holder (TCC-100) and a six-cell thermoelectrically temperature-controlled cell positioner (CPS-100) were used.[1)]

■ Solvatochromism (Solvent-Dependent Change)

Fig. 1 shows solutions of cobalt chloride dissolved in a variety of solvents. Cobalt chloride was dissolved in pure water and methanol at 6 g/L and in ethanol and acetone at 0.6 g/L. As shown in Fig. 1, solutions of cobalt chloride have different colors depending on the solvent, and it is believed that the variation in color are caused by the formation of either mainly tetrameric (blue) or octameric (pink) complexes, as shown in Equation (1).

Fig. 1 Solutions of Cobalt Chloride
Solvents from left to right: pure water, methanol, ethanol, and acetone

$$[CoCl_2(Solvent)_2](tetrameric) + 4Solvent \leftrightarrows [Co(Solvent)_6]^{2+}(octameric) + 2Cl^-(solvated) \quad \text{Equation (1)}$$

A UV-VIS spectrophotometer was used to measure the transmittance spectra of each solution. The measurement conditions used are shown in Table 1, and the measured spectra are shown in Fig. 2.

Table 1 Measurement Conditions

Instrument:	UV-2600i, TCC-100, STJ-0184 nitrogen gas generator
Wavelength Range:	380–780 nm
Data Interval:	1.0 nm
Scan Speed:	Medium
Slit Width:	1.0 nm

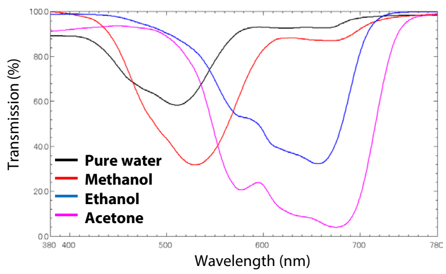

Fig. 2 Transmission Spectra of Cobalt Chloride Solutions (20 °C)

By examining transmission spectra, it can reveal how absorbed wavelengths differ depending on the solvent.

So the spectra were used to calculate the color values (the XYZ color system — chromaticity coordinates x and y), which were plotted as chromaticity coordinates (Fig. 3).

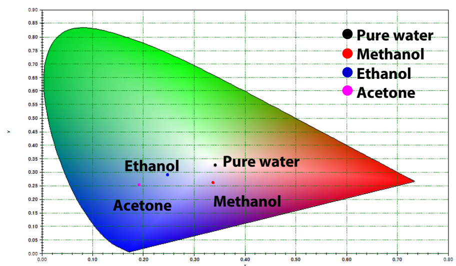

Fig. 3 Color Values of Cobalt Chloride Solutions (20 °C)

The optional color calculation software for Shimadzu's UV-Vis spectrophotometer control software (LabSolutions™) was used to display the measured spectra as chromaticity coordinates and provide a quantitative representation of the color of each sample.

■ Thermochromism (Temperature-Dependent Change)

The cobalt chloride solutions in the four different solvents, which were used above to measure solvatochromism were then measured at 10 °C increments between 10 and 50 °C. Fig. 4 shows the cobalt chloride solutions at 50 °C.

Fig. 4 Cobalt Chloride Solutions (50 °C)
Solvents from left to right: pure water, methanol, ethanol, and acetone

In methanol, the ratio of tetrameric (blue) to octameric (pink) complexes changed to produce a purple color, while in ethanol it produced a deeper blue color. These color changes represent a move to the left side of Equation (1). In pure water, cobalt chloride appeared to remain on the right side of Equation (1) and showed almost no change in color. In acetone, cobalt chloride formed the complexes shown in Equation (2)[1] and showed no change in color.

$$2[CoCl_2(Solvent)_2](tetrameric) + 2Solvent \leftrightarrows [CoCl_3(Solvent)]^-(tetrameric) + [CoCl(Solvent)_5]^+(octameric)$$

Equation (2)

Next are presented the results from measuring solution absorbance at 10 °C intervals between 10 and 50 °C. Fig. 5 shows the absorbance spectra obtained at 50 °C. The TCC-100 used a Peltier element to perform thermoelectric cooling, which provides easy control over the temperature without the need for cooling water. Measurements at sample temperatures below ambient required a supply of dry air to prevent condensation forming on the surface of the sample cell.

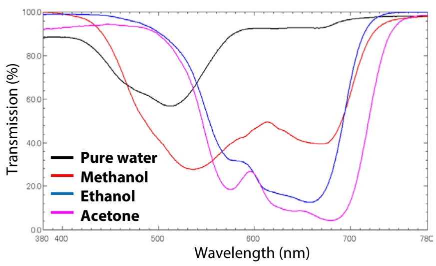

Fig. 5 Transmission Spectra of Cobalt Chloride Solutions (50 °C)

Comparing Fig. 2 and Fig. 5 reveals no temperature-dependent change in the spectral line shape in pure water and acetone, but it shows an increase in absorption at around 650 nm that accompanied the increase in temperature in methanol and ethanol. The change in the spectral line shape was presumably due to cobalt chloride complexes in solution transitioning from an octameric to a tetrameric form.

Next, color values were calculated at each temperature and represented as chromaticity coordinates (Fig. 6).

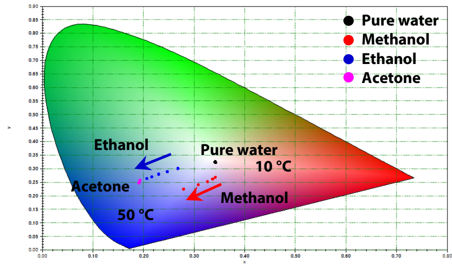

Fig. 6 Color Value of Cobalt Chloride Solutions at Each Temperature

Fig. 6 shows the gradual change in color of the cobalt chloride solution in methanol and ethanol as the temperature increased.

■ Thermochromism (Temperature-Dependent Change in a Solvent Mixture)

The thermochromism of cobalt chloride in solution was then measured in a solvent mixture of pure water and acetone. Solutions containing 6 g/L of cobalt chloride were prepared in five solvent mixtures with ratio of pure water and acetone ranging from 1:1 to 1:5. Using the CPS-100 to control the temperature of multiple samples concurrently, sample temperatures were varied between 20 and 60 °C and solution absorption was measured at 10 °C intervals (Table2).

Table 2 Measurement Conditions

Instrument:	UV-2600i, CPS-100
Wavelength Range:	380–780 nm
Data Interval:	1.0 nm
Scan Speed:	Medium
Slit Width:	1.0 nm

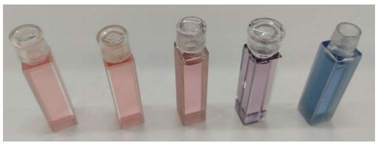

Fig. 7 Solutions of Cobalt Chloride (Room Temperature)
Pure water to acetone solvent ratios from left to right: 1:1, 1:2, 1:3, 1:4, and 1:5

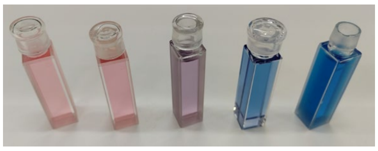

Fig. 8 Cobalt Chloride Solutions (60 °C)
Pure water to acetone solvent ratios from left to right: 1:1, 1:2, 1:3, 1:4, and 1:5

Figs. 7 and 8 show the samples at room temperature and at 60 °C, respectively, and Figs. 9 and 10 show the absorbance spectra obtained from the samples at 20 °C and 60 °C, respectively. Although the color of the 1:1 and 1:2 solvent ratio samples are difficult to differentiate by eye, the difference in color is identifiable in the spectra shown in Figs. 9 and 10.

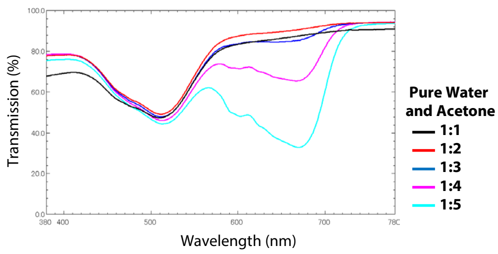

Fig. 9 Transmission Spectra of Cobalt Chloride Solutions (20 °C)

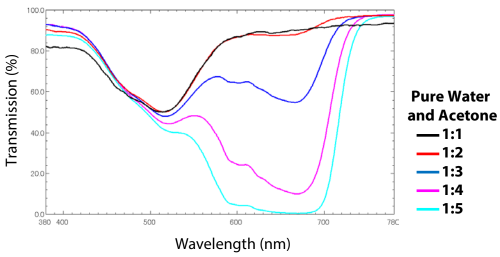

Fig. 10 Transmission Spectra of Cobalt Chloride Solutions (60 °C)

Next, color values were calculated at each temperature and represented as chromaticity coordinates (Fig. 11). Fig. 12 shows a magnified view of Fig. 11 with only the 1:1, 1:2, and 1:3 pure water and acetone solvent ratio samples displayed.

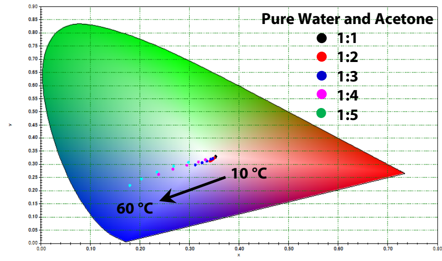

Fig. 11 Color Value of Cobalt Chloride Solutions at Each Temperature

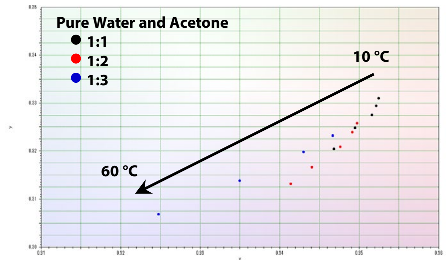

Fig. 12 Magnified View of Fig. 11

Fig. 12 shows how color changes that were difficult to distinguish by eye are clearly distinguishable when represented in terms of color values.

■ Conclusion

This Application News evaluated the solvatochromism and thermochromism of solutions of cobalt chloride. The changing of colors due to solvatochromism was evaluated quantitatively using the optional color calculation software for LabSolutions UV-Vis. The TCC-100 enabled the examination of thermochromism over the wide temperature range of 10 to 50 °C. The CPS-100, which can control the temperature of multiple samples concurrently, enabled a more efficient investigation of thermochromism.

This shows how selecting the right equipment for the application enables optimal temperature-controlled measurements.

<References>

1) Harada K. and Fukuda Y. Chromotropism of coordination compounds. Shigen-to-Sozai. Vol. 111, 523–530 (1995)

> Please fill out the survey

Related Products

Some products may be updated to newer models.

> UV-1900i

UV-VIS Spectrophotometer

> UV-2600i, UV-2700i

UV-VIS-NIR Spectrophotometer

> UV-3600i Plus

UV-VIS-NIR Spectrophotometer

Related Solutions

> Engineering Materials

> Optical Materials

> Price Inquiry

> Product Inquiry

> Technical Service / Support Inquiry

> Other Inquiry