

Spectroscopic Investigation of Complexes of Morin with Alum

Chutima Septhum [a], Saowanee Rattanaphani [a], John B. Bremner [b]
and Vichitr Rattanaphani [a]

[a] School of Chemistry, Suranaree University of Technology, Nakorn Ratchasima,
Thailand, 30000.

[b] Institute for Biomolecular Science and Department of Chemistry, University of
Wollongong, Wollongong, Northfields Avenue, NSW 2522, Australia

Abstract

Morin one of the substances found in some yellow natural dyes is a phenolic compound derived from hydroxyl substitutions on the flavone chromophore. This flavone-based compounds are known to form stable complexes with metal cations [1-6]. In this work complex formation between alum and morin in water was studied by using spectroscopic measurements. It was shown that morin molecule forms alum-morin (3:2) complex. The complex is a deep-yellow chelate which has UV-Vis absorption maximum at 415 nm. Increasing the alum concentration caused a bathochromic shift of morin band in alum-morin complex. The study also indicated that when the concentration of alum increased within the range of concentration (0-250 μM) studied, the intensity of the long wavelength absorption band of morin-alum complex increased accordingly.

Keyword: Morin; Spectroscopic; Complexation; Alum; Stoichiometry

Introduction

Flavonoids, polyphenolic pigments widely present in plants. Morin (3,5,7,2',4'-pentahydroxyflavone) is a phenolic compound derived from hydroxyl substitutions on the flavone chromophore. Fig. 1 shows the chemical structure of morin. The flavone-based compounds are known to form stable complexes with metal cations [1-6]. Morin can selectively form highly colored and fluorescent complexes with metal ions which has been explored in analytical methods of metal [1]. Morin association with Al has focused attention on the investigation of the stoichiometry of the complexes and determination of possible sites of binding [2]. Stoichiometry of the complexes of Al(III) with morin are Al(Morin) and Al(Morin)₂ in methanol. Alum widely used as mordant for dyeing keratin fibres with polyphenolics dye to obtain the bright colour rendition and wash-fast finish. However, the stoichiometry of complexes of alum with morin in water have not been reported yet.

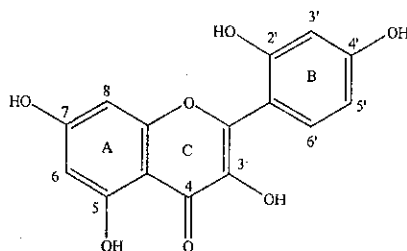


Fig. 1 Chemical structure of morin

The aim of the work is to determine the stoichiometric composition of the complex formed between morin and alum in water. The molar ratio method is used for the spectrophotometric determination of the complex.

Materials and Methods

Morin [480-16-0] was purchased from Sigma. Alum ($KAl(SO_4)_2 \cdot 12H_2O$) and methanol were obtained from the Merck. The morin stock solution (1.0×10^{-3} M) is prepared successively in 50% (v/v) methanol. Alum solutions are prepared in distilled water. The stoichiometry of complexes was determined by the molar ratio method. A concentration of 5.0×10^{-5} M of morin in water was diluted from stock solution and kept constant whereas alum was varied from 0 to 250 μ M. The pH values were measured using pH meter (Schott). In order to reach the complexation equilibrium, the absorption spectra of each solution was recorded after standing 30 minutes. An Agilent 8453 UV-Vis spectrophotometer was employed for absorbance measurements using quartz cells of path length 1 cm.

Results and discussion

The UV-Vis spectrum of morin in water (Fig. 2) is characterized by two major absorption bands with maxima at 378 nm (band I) and 261 nm (band II). Band I is considered to be associated with the absorption due to the B-ring cinnamoyl system, and band II with the absorption involving the A ring system. The absorbance of band I of morin decreases at 378 nm and a new band, which increases with the amount of added alum, appear at 415 nm.

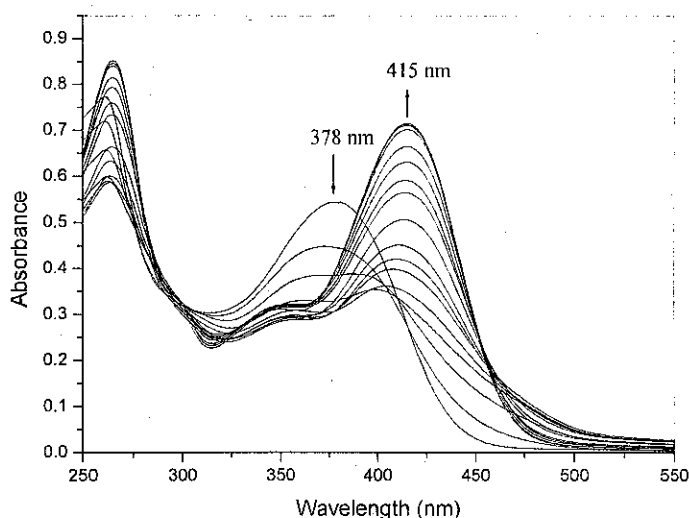


Fig. 2. Electronic absorption spectra of morin (5.0×10^{-5} M) in water in absence and in presence of alum (0-250 μ M)

The stoichiometry of Al-morin complexes depend on media such as solvent and pH. The association of Al^{3+} with morin gives rise two complexes with 1:1 and 1:2 (Al^{3+} : morin) stoichiometries in methanol solution and 1:1 in acidic methanol solution. The main sites of Al (III) binding to morin is shown in the molecular model of Fig. 3 [2].

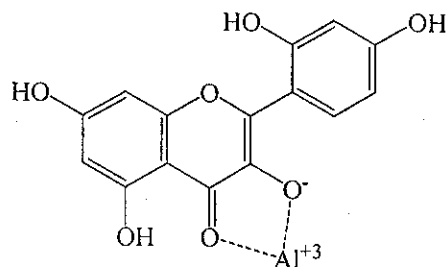


Figure 3. Molecular models of Al(III) complexation with morin

In this study the stoichiometry of the complex was determined applying the molar ratio method. The molar ratio plots at 415 nm (λ_{\max} of complex) shows inflection at $[\text{alum}]/[\text{morin}] = 1.5$, indicating a stoichiometry alum: morin of 3:2 for complex (Fig. 4). The pH range of final solution was 5.33-4.07. The possible structure for alum-morin is shown in Fig. 5. Morin possesses two possible chelating sites, 3-hydroxy-4-oxo and 5-hydroxy-4-oxo systems. In addition, the 3,2'-dihydroxy system in morin is a potential chelating site, which is so placed that a seven-membered chelate ring is formed on binding Al ion. An Al ion bridges 2'- and 3-hydroxy groups rather than 4-keto- and 3-hydroxy groups, and makes another Al ion binding with 5-hydroxy-4-oxo system possible (Fig. 5). Future modeling study to support the proposed structure is on the way.

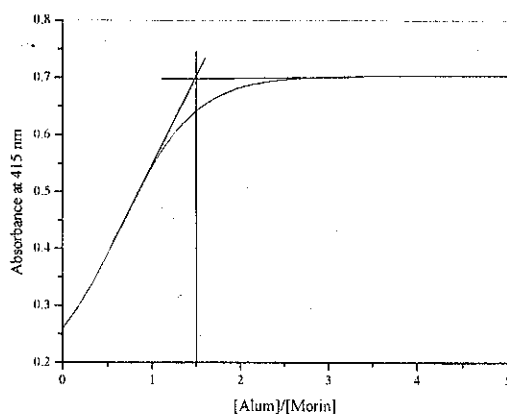


Fig. 4. Absorbance versus $[\text{alum}]/[\text{Morin}]$ molar ratios plots at 415 nm.

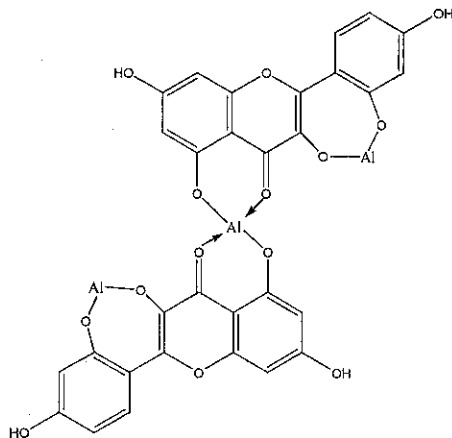


Figure 5. Possible structure of Al(III) complexation with morin

The result of the study of alum effect on the visible spectra (λ_{\max}) of morin is presented in Fig. 6 which indicated the large bathochromic shift of morin as the alum concentration increased.

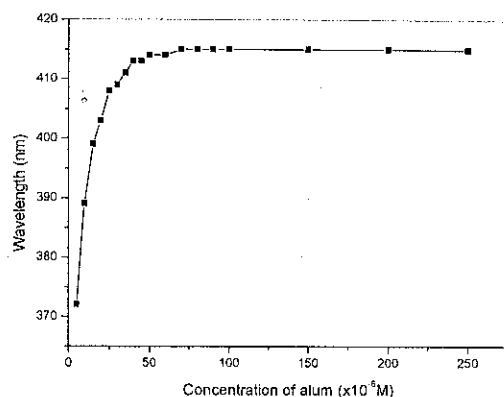


Fig. 6. The effect of alum concentrations on the absorption band of morin.

The higher alum concentration presumably results in stronger interaction with morin and the intensity of the long wavelength absorption band of morin also increased.

Conclusions

The UV-Vis spectra of morin in water exhibit two main absorption bands at 378 and 261 nm. Applying the molar ratio method, it was determined that stoichiometric composition of complex formed is $\text{Al}_3(\text{morin})_2$. Increasing the alum concentration caused a bathochromic shift of the visible absorption bands.

Acknowledgements

We gratefully acknowledge support from Suratthani Rajabhat University and Suranaree University of Technology for Chutima Septhum.

References

1. M. J. Ahmed and J. Hossan, *Talanta*, Vol. 42, 1995, p.1135.
2. A. C. Gutierrez and M. H. Gehlen, *Spectrochimica Acta Part A*, Vol. 58, 2002, p.83.
3. A. C. Boudet, J. P. Cornard and J. C. Merlin, *Spectrochimica Acta Part A*, Vol. 56, 2000, p.829.
4. J. P. Cornard and J. C. Merlin, *Journal of Molecular Structure*, Vol. 569, 2001, p.129.
5. G. T. Castro and S. E. Blanco, *Spectrochimica Acta Part A*, Vol. 60, 2004, p.2235.
6. J. P. Cornard and J. C. Merlin, *Journal of Inorganic Biochemistry*, Vol. 92, 2002, p.19