# Spectrophotometric determination of preferential solvation and solvation shell composition of morin hydrate in some water-aliphatic alcohol mixed solvents

Rahil Yazdanshenas, Farrokh Gharib *

*Chemistry Department, Shahid Beheshti University, G. C., Evin, Tehran, Iran*

A B S T R A C T

Absorption spectra of a flavonoid (morin hydrate) were studied in pure water, methanol, ethanol, 1-propanol, and 2-propanol and also in their aqueous binary mixtures at 25.0 °C. Spectral changes were interpreted in terms of specific and non-specific solute-solvent interactions. The molar transition energy ($E_T$) in the maximum absorption as a solvatochromic probe was measured in each binary mixture. The local mole fraction of each solvent composition calculated in the cybotactic region of the probe. The extent and importance of each solute-solvent interaction to $E_T$ was analyzed in the framework of the linear solvation energy relationships. Preferential solvation was detected as a non-ideal behavior of $E_T$ curve respective to the mole fraction of the alcohols in all the binary mixtures. The preference of morin hydrate to be solvated by one of the solvating species relative to the others was discussed in terms of solvent-solvent and solute-solvent interactions.

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## 1. Introduction

Aqueous-organic mixed solvents are usually and widely used to dissolve many insoluble or sparingly soluble compounds [1–2]. In such solutions, solute molecules interact differently with each of the solvent components and so a preferential solvation process occurs [3]. The solvent composition in the near vicinity of a solute molecule (local composition) can be significantly different from the bulk composition [4]. In this case both solute-solvent and solvent-solvent interactions have significant roles in determining the preferential solvation process [5–7]. Studying solute-solvent and solvent-solvent interactions and how they affect the structure of a solute is of interest and has a major role in all phenomena in liquid phases. One of the most important properties of a solvent is its polarity, which has a great effect on chemical reactions. Sometimes, it seems to be more favorable to define "solvent polarity" as the overall solvation capability, which is the cumulative effect of all possible, specific and nonspecific, intermolecular interactions between solute and solvent molecules [3].

Preferential solvation phenomena have been extensively studied for binary solvent mixtures. These include experimental studies based on thermodynamic [8], IR [9–10], NMR [11], or UV–Vis measurements [5–7,12–14] and theoretical approaches such as molecular dynamics [15–16], Monte Carlo calculation [17], and molecular solvation theory [18–19]. However, the most widely and successfully applied method in preferential solvation studies is the measurement of molar transition energies by UV–Vis spectroscopy of molecular solute probes, which their absorption bands undergo shifts depending on the solvent composition (solvatochromism phenomena) [20]. The electronic transition energy of the solvatochromic solute at the absorption maximum depends on the composition of the probe's solvation shell and can be used to quantify the polarity of the solvent in the cybotactic region of the solute molecules. The polarity scale, $E_T$, is comprised of all sorts of interactions between solute and solvent components and can therefore reveal the nature of solute-solvent as well as solvent-solvent interactions present in the mixtures.

In the present work, the UV–Vis spectrophotometric technique has been used to study the preferential solvation, solute-solvent interactions, of morin hydrate in pure methanol, ethanol, 1-propanol, and 2-propanolas well as in their corresponding binary aqueous mixtures at 25.0 °C.
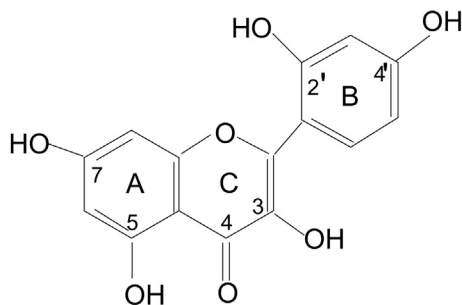
## 2. Experimental

### 2.1. Materials and method

All solvents were from Merck (HPLC grade) and used as received. Morin hydrate ($C_{15}H_{10}O_7$, x$H_2O$), (3, 5, 7, 2′, 4′- penta-hydroxy flavone), Scheme 1, supplied from Sigma and used without further purification. The number of water molecules attached to one morin molecule was

* Corresponding author.
  *E-mail address:* f-gharib@sbu.ac.ir (F. Gharib).

**Scheme 1.** Chemical structure of morin.

determined $(x = 2)$ using Karl-Fisher procedure [21]. The purity of morin hydrate was checked by alkalimetric titration method. All solutions and dilution processes were performed using double-distilled water with a conductance equal to $2.0 \pm 0.1$ μS.

A stock solution of morin hydrate $(1.0 \times 10^{-3}$ mol·dm$^{-3})$ was prepared in 1-butanol. In a series of volumetric glass tubes, 60 μL of the stock solution of morin hydrate was transferred. After evaporation of the organic solvent in the tubes under reduced pressure, 3 mL of pure alcohols or aqueous binary solvent mixtures was pipetted into the tubes and the mixtures were sonicated to form a clear and homogenous solution. All aqueous binary mixtures were carefully prepared by weighing at the required molar ratio with an electrical balance to $\pm 0.01$ mg. The final concentration of the solute in the tubes was obtained $2.0 \times 10^{-5}$ mol·dm$^{-3}$. Due to the very low solubility of morin hydrate in pure water, only 9 μL of the morin hydrate stock solution was transferred to one of the tubes to allocate it to pure water. Spectral measurements were performed with a Shimadzu UV–Vis 2100 spectrophotometer, using thermostated matched 10 mm quartz cells at $25.0 \pm 0.1$ °C. The electronic absorption spectra of morin hydrate were recorded over the wavelength range of 300–450 nm at a rate of 20 nm·min$^{-1}$ with a slit width of 5 nm. At least three replicate spectrophotometric measurements were done for each solution with an accuracy of $\pm 0.05$ nm. The maxima on the UV–Vis spectra $(\lambda_{max})$ were determined from the first derivative of absorption spectrum and were then used to calculate $E_T$ values.

## 3. Preferential solvation model

One of the most convenient and successful methods in preferential solvation studying is the solvent exchange model developed by Bosch and her co-workers [21–23]. This model extended the stepwise solvent exchange model of Connors and co-workers [24] to equations that relate the electronic transition energy values of the solvatochromic probes with the solvent composition. The present equations involve preferential solvation parameters that consider the solute-solvent as well as solvent-solvent interactions. In this basis, for a binary mixture composed of solvents 1 (S1, water) and 2 (S2, organic solvent) as well a solvatochromic indicator (I), the following equilibria for the solvent exchange processes are considered.

$$I(S1)_m + mS2 \rightleftharpoons I(S2)_m + mS1 \tag{1}$$

$$I(S1)_m + \frac{m}{2}S2 \rightleftharpoons I(S12)_m + \frac{m}{2}S1 \tag{2}$$

I(S1) and I(S2) represent that the solute I is fully solvated by the solvents S1 and S2, respectively. Further, the solvent molecules can also interact with each other to form a solvating complex as S12 [22]. In this model, it is proposed that the solvating complex (S12) has a different property from S1 and S2 and the composition of the solvation shell in the vicinity of the solute molecules (local composition) are in equilibrium with the bulk composition of the mixed solvents [21]. Here, $m$ is

interpreted as the number of solvent molecules involved in the exchange process in the solvation shell of the solvatochromic probe and should not be confused with the total number of molecules that solvate the indicator [23].

The constants of the exchange equilibria of Eqs. (1) and (2) are defined by the preferential solvation parameters $(f_{2/1}, f_{12/1},$ and $f_{12/2})$ which are related to the solvent mole fraction in the local shell of the probe, $x_1^L, x_2^L,$ and $x_{12}^L$, as well as to their mole fractions in the bulk mixtures, $x_1^B$ and $x_2^B$.

$$f_{2/1} = \frac{x_2^L}{x_1^L} \left(\frac{x_1^B}{x_2^B}\right)^m \tag{3}$$

$$f_{12/1} = \frac{x_{12}^L}{x_1^L} \left(\frac{x_1^B}{x_2^B}\right)^{m/2} \tag{4}$$

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} = \frac{x_{12}^L}{x_2^L} \left(\frac{x_2^B}{x_1^B}\right)^{m/2} \tag{5}$$

The preferential solvation parameter, $f_{i/j}$, represents the tendency of solute I to be solvated by solvent i in the presence of solvent j. The interpretation of preferential solvation parameters can be made using the Bosch model [22]. On this basis, values of $f_{i/j}$ close to 1 indicate an ideal mixture and no preferential solvation by the solvents; values lower than unity imply a preferential solvation of the indicator I by solvent j in comparison with solvent i, and the opposite is true if the values are higher than 1.

The electronic transition energy, $E_T$, of a solvatochromic solute in a mixture results from the sum of the contributions of each solvent entity in the cybotactic region, which is represented by the product of its mole fraction by the property value of that entity. Therefore:

$$E_T = E_{T1}x_1^L + E_{T2}x_2^L + E_{T12}x_{12}^L \tag{6}$$

where $E_{T1}$, $E_{T2}$, and $E_{T12}$ represent the values of $E_T$ when the solute is solvated by S1, S2, and S12, respectively.

Assuming that the sum of all mole fraction species present in the solvation shell should be equal to unity, the solvent mole fraction in the local shell of the probe can be calculated from Eqs. (3) and (4):

$$x_1^L = \frac{(x_1^B)^m}{(x_1^B)^m + f_{2/1}(x_2^B)^m + f_{12/1}(x_1^B)^{m/2}(x_2^B)^{m/2}} \tag{7}$$

$$x_2^L = \frac{f_{2/1}(x_2^B)^m}{(x_1^B)^m + f_{2/1}(x_2^B)^m + f_{12/1}(x_1^B)^{m/2}(x_2^B)^{m/2}} \tag{8}$$

$$x_{12}^L = \frac{f_{12/1}(x_1^B)^{m/2}(x_2^B)^{m/2}}{(x_1^B)^m + f_{2/1}(x_2^B)^m + f_{12/1}(x_1^B)^{m/2}(x_2^B)^{m/2}} \tag{9}$$

Finally, by introducing Eqs. (7)–(9) into Eq. (6), a general equation is derived for determination of $E_T$ value.

$$E_T = \frac{E_{T1}(x_1^B)^m + f_{2/1}E_{T2}(x_2^B)^m + f_{12/1}E_{T12}(x_1^B)^{m/2}(x_2^B)^{m/2}}{(x_1^B)^m + f_{2/1}(x_2^B)^m + f_{12/1}(x_1^B)^{m/2}(x_2^B)^{m/2}} \tag{10}$$

## 4. Results and discussion

The UV–Vis absorption spectra of morin hydrate were recorded in several HBD solvents with strong hydrogen-bond donor capabilities. Fig. 1 shows the spectra of morin hydrate in pure water, methanol, ethanol, 1-propanol, and 2-propanol. The spectra in Fig. 1 exhibit one broad