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SPECTRAL METHODS TO ESTIMATE THE STRENGTH OF INTERMOLECULAR INTERACTIONS IN LIQUIDS

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INTRODUCTION

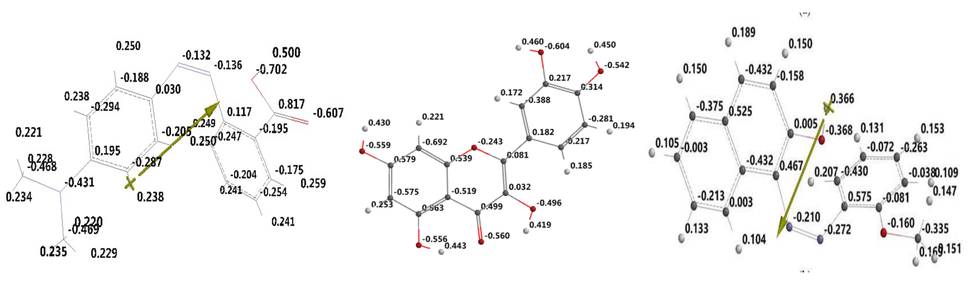
The spectrally active molecules are used in very small quantities as probes which measure the local field in liquids by the modifications induced in their electronic spectra. The energetic levels of the molecules participating to the electronic transitions are stabilized in solvation process. When the solvation energy differs in the two states of the electronic transition, the spectral shifts of the electronic bands offer information about the strength of the solute-solvent interactions.

The linear dependences between the spectral shifts of the electronic bands and the solvent parameters are used to compute the contributions of each type of intermolecular interactions at the solvation energy.

The spectral methods are applied to separate the contribution of the universal and specific interactions in simple and complex liquids. Both non-polar and polar spectrally active molecules are used in this study to evidence the intermolecular interactions in various solvents.

Materials and methods

Three spectrally active molecules were analyzed:



a) b) c)

Fig. 1 Optimized structure of methyl-red (a), quercetin (b), Sudan red G (c)

The studied molecules were purchased from Sigma–Aldrich and used without further purification. Spectral grade solvents were purchased from Merck and Sigma-Aldrich (most ACS reagent or Reagent Plus, with purity exceeding 99%).

Electronic absorption spectra of methyl red were recorded in 14 solvents at room temperature using a QE65000 UV-Vis Ocean-Optics spectrometer. The statistical analysis of the solvatochromic data was performed using Origin Pro 9 software. Spartan'14 software was used to compute the molecular structures, vibrational frequencies, and energies of optimized structure of the studied molecules.

In a multiple parameter approach, a linear solvation energy relationship may be described by

$$\upsilon_{calc.} = \upsilon_0 + C_1 f(\varepsilon) + C_2 f(n) + C_3\beta + C_4\alpha$$

where:

$$f(n) = \frac{n^2 - 1}{n^2 + 2} \qquad f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2}$$

β and α are Kamlet, Abboud and Taft parameters.

RESULTS AND DISCUSSION

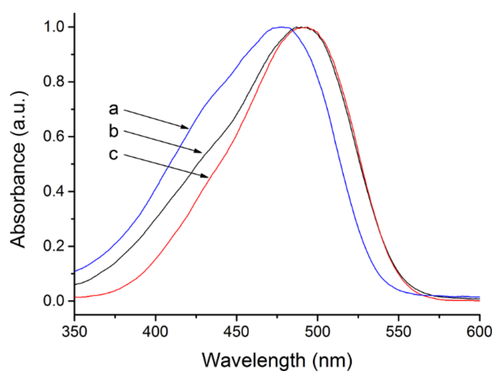


Fig. 2. Visible electronic absorption band of 10^{-5}mol /l methyl red in (a) dioxane, (b) 2-butanol and (c) dichloroethane

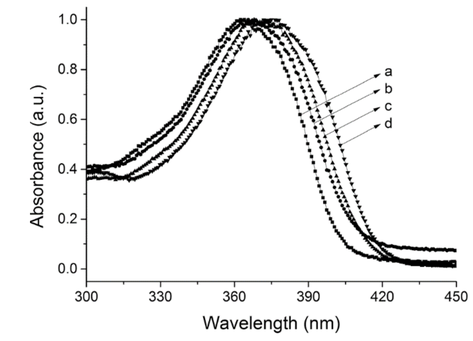
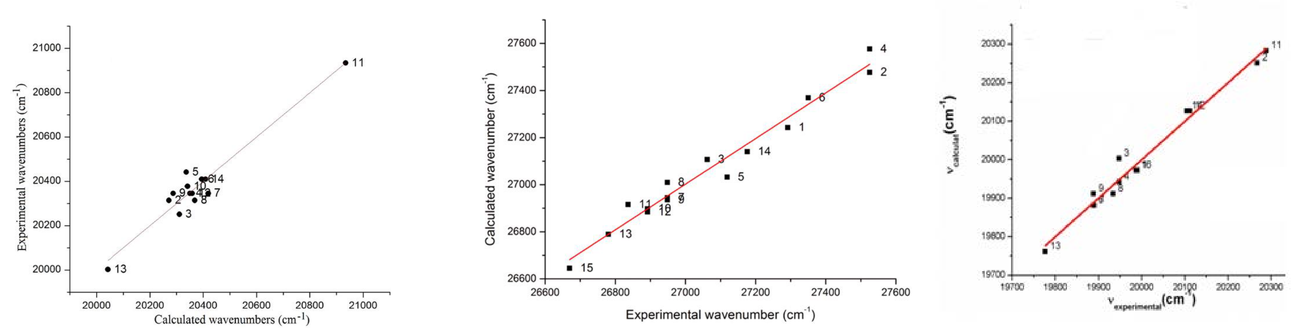
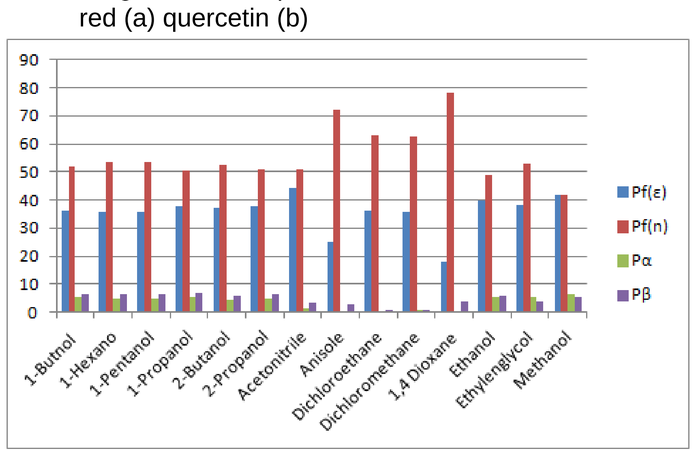


Fig. 3. Ultraviolet-visible electronic absorption band of quercetin dissolved in (a) acetonitrile, (b) methanol, (c) 2-propanol, and (d) dimethyl sulfoxide (d). The concentration quercetin was approximately 10^{-4}mol/l

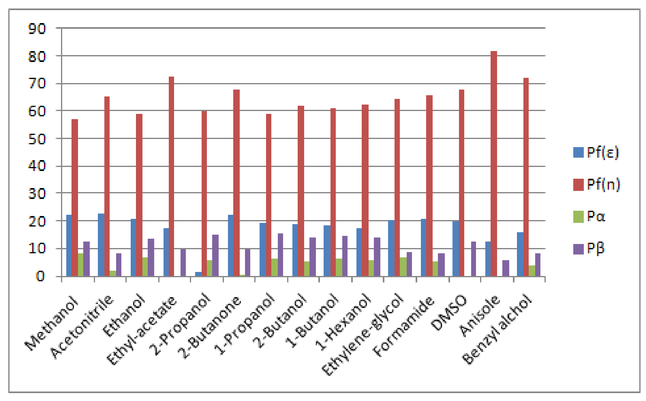


a) b) c)

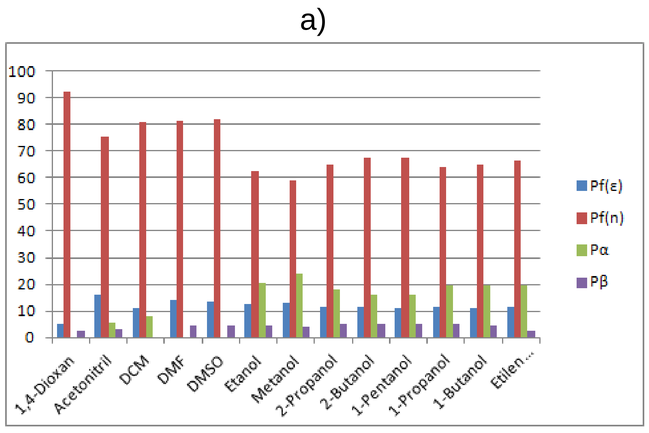
Fig. 4 Linear dependence between calculated wavenumbers and experimental wavenumbers for methyl red (a) quercetin (b)



a)



b)



c)

Fig. 5 Contribution of each type of interaction to the total spectral shifts for methyl red (a) quercetin (b) and Sudan red G (c)

CONCLUSIONS

The contribution of various intermolecular interactions to the spectral shifts of the electronic absorption band of methyl red was evaluated by performing multiple linear regression analysis of the dependence between the wavenumbers in the maxima of the spectral band and solvent parameters.

The dispersion interactions are predominant in the binary solutions the studied molecules.

The protic solvents donate protons to achieve hydrogen bonds with the negatively charged atoms of spectrally active molecules. Hence, the contribution of specific interactions to the total spectral shifts is higher in protic solvents than in the aprotic ones.

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