



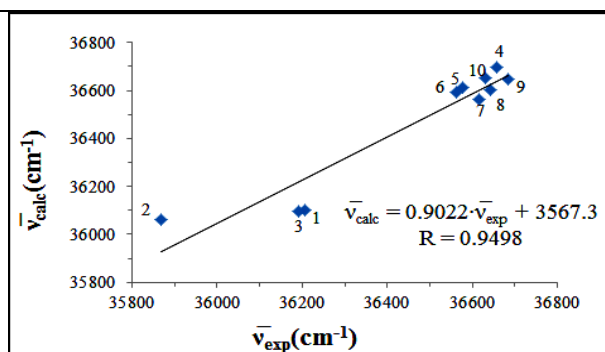
UNIVERSAL AND SPECIFIC INTERACTIONS IN CAFFEINE DILUTED SOLUTIONS

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Received July 7, 2015

This paper is focused on the interactions developed in caffeine solutions with different polarity solvents in order to identify universal type interactions as well as specific ones. The numerical analysis of spectral data was performed by multiple linear regression algorithms considering the spectral shift of electronic absorption bands recorded in caffeine solutions and various functions of solvent parameters. The study revealed the contribution of both universal (dipole-dipole orientation forces and dispersive ones) as well as the contribution of hydrogen bond formation. Solvent box approach applied by means of quantum chemical calculation confirmed the role of hydrogen bonds in protic solvent solutions of caffeine.



INTRODUCTION

The basic interpretation of the dependency of electronic absorption bands (EAB) wavenumber on the solvent macroscopic parameters was accomplished by several researchers like McRae and Kamlet – Taft, known for their solvatochromic theories.¹⁻³ Equation (1) represents the simplified McRae's formula deduced from his solvatochromic theory,¹⁻⁷ where $\bar{\nu}_0$ is the wavenumber of the electronic transition of molecule in isolated state, ϵ and n represent the dielectric constant and refractive index of the solvent while A and B are the coefficients proportional to the strength of the induction-dispersive and orientation interactions, respectively (that depend on microscopic parameters of solute and solvent molecules).

$$\bar{\nu}_{max} = \bar{\nu}_0 + A \cdot \left[\frac{n^2 - 1}{2n^2 + 1} \right] + B \cdot \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (1)$$

The spectral shift caused by the solvent effect was described by Kamlet-Taft approach³ using α , β and π^* empirical solvent parameters (eq. 2), where α is the solvent hydrogen bonding acidity (i.e. hydrogen bonding donating ability), β is the solvent bonding basicity (or hydrogen bonding accepting ability) and π^* is the solvent dipolarity/polarizability parameter:

$$\bar{\nu}_{calc} = \bar{\nu}_0 + a\alpha + b\beta + s\pi^* \quad (2)$$

The coefficients of α and β parameters express the contribution of specific interactions to the total shift observed in EAB while the contributions of the universal interactions are expressed by the coefficient of π^* – all possible universal forces being grouped under this parameter. Other studies can be mentioned related to spectral data analysis based on various solvatochromic theories where also estimation of

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solute microscopic electro-optical parameters was accomplished.⁸⁻¹⁷

The below study is a comparative approach of caffeine-solvent interactions effect on the EAB wavenumbers developed based on each of the above mentioned theories using multiple regression algorithms.

RESULTS AND DISCUSSION

By applying quantum chemical modeling the optimized geometry of caffeine molecule in Fig. 1 A can be seen while in Fig. 1 B the electrostatic potential distribution around atoms constituting caffeine molecule are presented – the contiguous line representing the positive electrostatic potential curves and dashed line the negative electrostatic potential.

Most significant electric charge density was revealed around the nitrogen (-0.133) and oxygen (-0.379) atoms where possible intermolecular interactions could be located further when protic solvent is added (Fig. 1 B). The dipole moment direction in the ground state was estimated to be in the main molecule plan and its value was found of 3.904 D. The electronic absorption spectrum (EAS) of optimized caffeine molecule – in isolated state (*i.e.* in the vapor state) is given in Fig. 2 A. The near UV band maximum is around 31000 cm⁻¹ while the far UV band maximum is approximately at 43,000 cm⁻¹. The caffeine EAS recorded in

water diluted solution (10⁻⁴ M) in Fig. 2B is presented. The two main band maxima (Fig. 2 B) were observed that have wavenumbers with several thousand cm⁻¹ more than for the isolated molecule in the vapor state (Fig. 2 A).

The values of the wavenumbers measured in the maxima of the two caffeine EABs were correlated with the solvent parameters aiming to evidence the presence of universal and specific solute-solvent interactions. First the application of McRae's formula (eq. 1) was done; for simplification, the two terms depending on solvent parameters were noted as $f(n)$ and $f(n, \epsilon)$; $f(n) = (n^2 - 1)/(2n^2 + 1)$ expressing the solvent shift due to dispersive – induction – polarization interactions while $f(n, \epsilon) = (\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)$ corresponds to the forces due to dipolar solute-solvent orientation interactions.

The solvatochromic shift on the basis of McRae's equation resulted in the graphs from Figs. 3 A, B. The factors A and B from eq. (1) were also numerically calculated for both bands (relations (3), (4)) through multiple linear regression approach against $f(n)$ and $f(n, \epsilon)$ functions from eq. (1), their absolute value representing the contribution of each interaction type to the total shift, while minus or plus sign represent the positive solvatochromic effect or, respectively, the negative solvatochromic effect. For the near UV band:

$$\bar{\nu}_{calc} = 37457.47 - 6831.60 \cdot f(n) + 638.33 \cdot f(n, \epsilon) \quad (3)$$

Different relation was found for the far UV band:

$$\bar{\nu}_{calc} = 56193.31 - 42922.34 \cdot f(n) - 731.98 \cdot f(n, \epsilon) \quad (4)$$

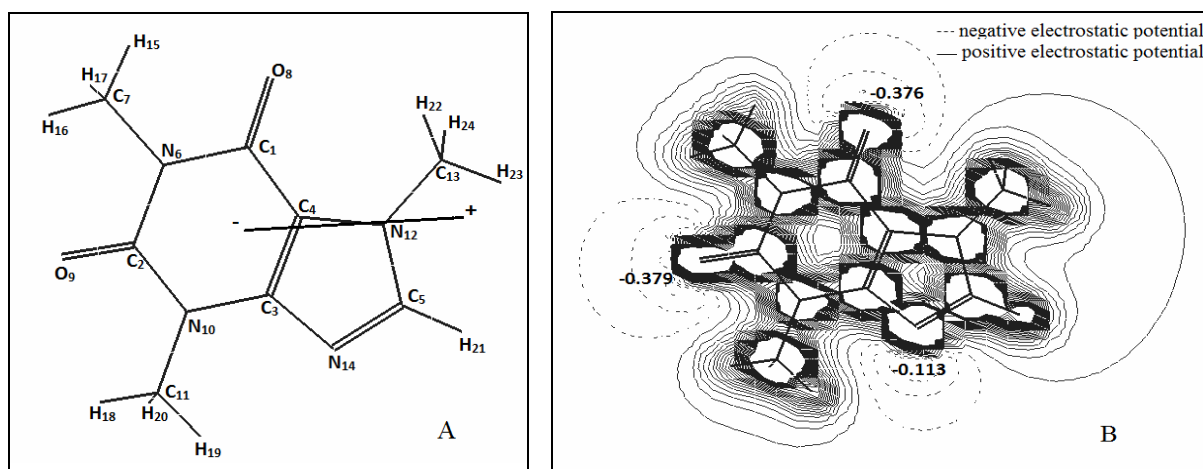


Fig. 1 – A. Caffeine optimized structure with dipole moment; B. Electrostatic potential distribution map.

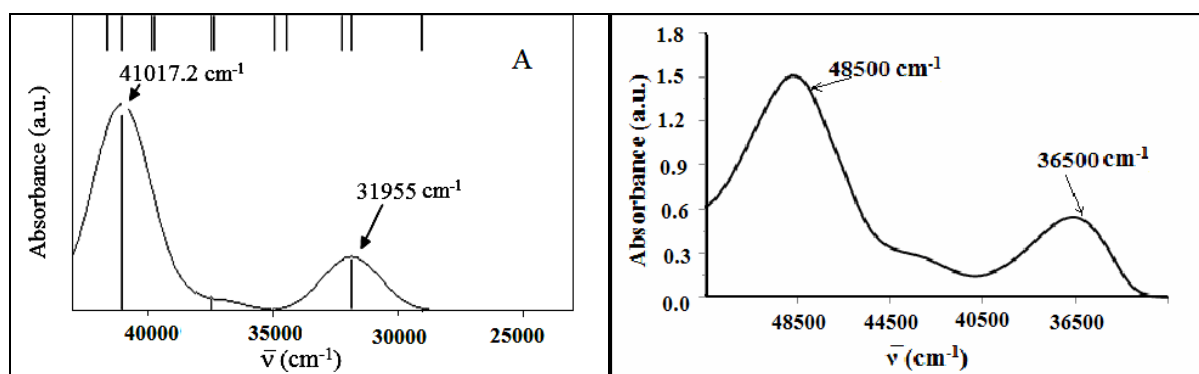


Fig. 2 – A. Simulated absorption spectrum of caffeine; B. The recorded spectrum of caffeine in water.

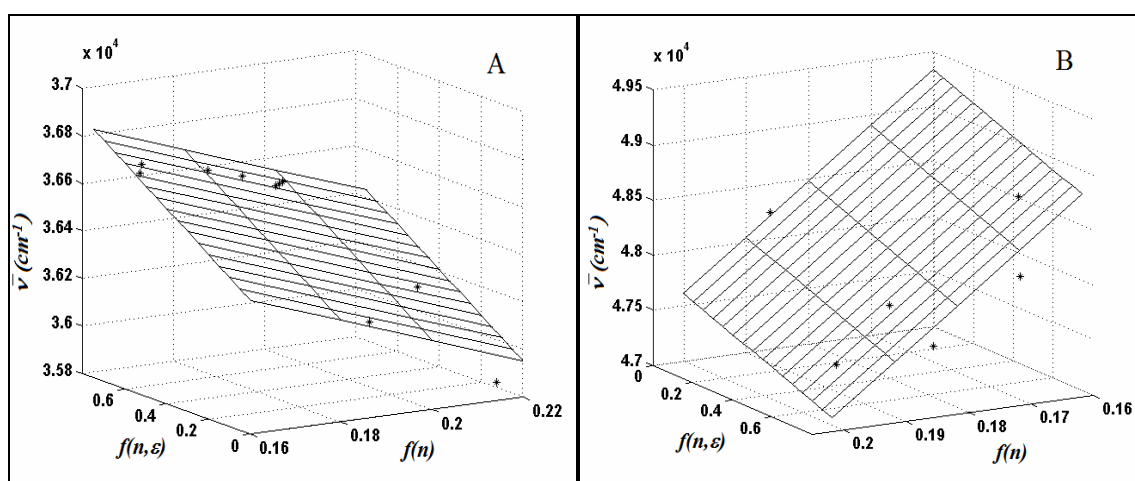


Fig. 3 – McRae regression plane. A. for the near UV band. B. for the far UV band.

Comparison of experimental wavenumbers and those calculated according to McRae's theory for the maxima of near UV band as well as for the far UV band was provided by the relations (4) and (5):

$$\bar{\nu}_{calc} = 0.8635\bar{\nu}_{exp} + 4976, R = 0.929; \quad (5)$$

$$\bar{\nu}_{calc} = 0.5607\bar{\nu}_{exp} + 21085, R = 0.749 \quad (6)$$

Lowest correlation coefficients, for the far UV band could be direct consequence of smaller number of solvents with such large transparency domain but also of the fact that only universal interactions were taken into account. Searching for higher correlations, another solvatochromic theory focused on universal interaction effects on the energy of the molecular electronic transitions was applied.

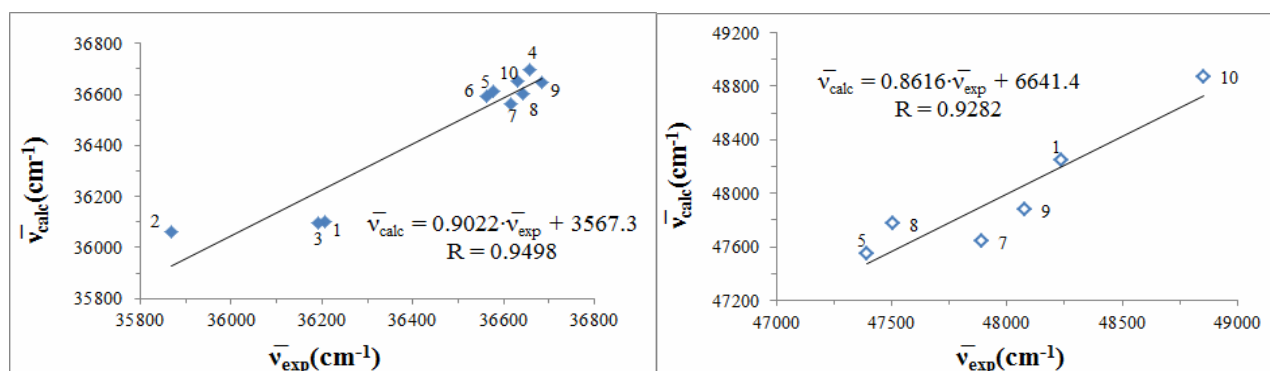


Fig. 4 – Comparison of experimental wavenumbers and those calculated according to Kamlet-Taft. A. for the near UV band; B. for the far UV band.

New approach was done aiming to include also the role of specific solute-solvent interactions as suggested by Kamlet-Taft theory.³ From the multiple regression based on Kamlet-Taft solvent

parameters, the following expressions (eq. (7), (8)) were deduced for the calculated maximum absorption bands in near UV and respectively in the far UV range:

$$\bar{\nu}_{calc} = 36083.13 + 587.30 \cdot \alpha + 139.08 \cdot \beta - 168.10 \cdot \pi^* \quad (7)$$

$$\bar{\nu}_{calc} = 48457.03 - 966.19 \cdot \alpha - 1198.58 \cdot \beta + 1934.56 \cdot \pi^* \quad (8)$$

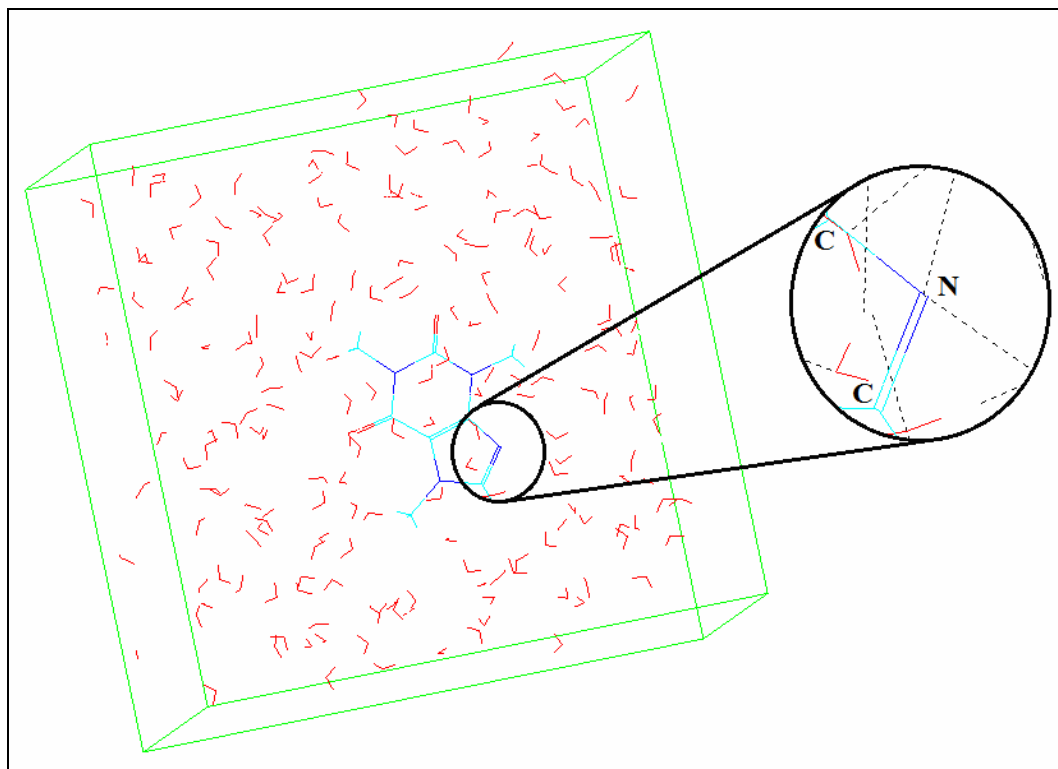


Fig. 5 – Hydrogen bond formation computed by Periodic Box modeling.

The relatively high regression coefficients, $R = 0.95$ for the near UV band (Fig. 4 A) and $R = 0.93$ for the far UV band (Fig. 4 B) – which are the highest among the two considered cases, suggested that indeed specific interactions as hydrogen bonds should to be considered, due to solvent capabilities – of donating and accepting hydrogen, with opposite solvatochromic effects than the universal interactions, i.e. the hydrogen bonds stabilizing more the ground state in the near UV transition and the exciting state in the far UV transition. The hydrogen bond formation was simulated by Periodic Box modeling in HyperChem.

The calculation was computed with the convergence limit and RMS gradient of 0.01 and the suggested size of the box side of 18.7 Å (203 water molecules). As shown in Fig. 5, there are two weak hydrogen bonds formed on unsaturated nitrogen atoms (dashed line in the scheme detail).

No significant change in caffeine dipole moment (4.014 D compared to 3.906 D) was caused by hydration. Further studies could be accomplished in ternary solutions^{15, 16} with protic/non-protic solvents.

From all above findings it appears that both large categories of solute-solvent interactions are important in caffeine solutions with protic solvents: universal and specific ones. Kamlet-Taft solvatochromic approach and quantum chemical modeling have shown that hydrogen bonds are present in the proximity of caffeine molecule together with volume dipole-dipole interactions. Other studies using Kamlet-Taft approach were reported in¹²⁻¹⁴ where electronic spectra in solvents with various polarities were used to identify intermolecular interaction mechanisms as well as dipole moments in the ground and excited states.

Table 1
Solvent parameters

No.	Solvent	ϵ	n	α	β	π^*
1	n-Hexane	1.88	1.3749	0	0	-0.11
2	Carbon tetrachloride	2.24	1.4602	0	0.10	0.21
3	Chloroform	4.89	1.4459	0.2	0.10	0.69
4	Acetic acid	6.20	1.0000	1.1200	0.45	1.00
5	n-Butanol	17.51	1.3993	0.8400	0.84	0.47
6	Isobutyl alcohol	17.93	1.3959	0.7900	0.84	0.41
7	Isopropyl alcohol	18.92	1.3772	0.7600	0.84	0.48
8	Ethanol	24.55	1.3614	0.8600	0.75	0.54
9	Methanol	32.66	1.3284	0.9800	0.66	0.60
10	Water	78.36	1.3333	1.1700	0.47	1.09

EXPERIMENTAL

Caffeine crystallized powder from Mayam, certified by Ecocert, France, was used to yield 10^{-4} M solutions with high purity solvents with large transparency domain purchased from SIGMA. Solvent parameters are given in Table 1. Deionized water prepared with Water Purification System Model Barnstead EASY Pure RODI was also used.

Spectral device used for experimental EAB recording was a SHIMADZU spectrophotometer provided with quartz cells. The semi-empirical quantum mechanics method PM3 implemented in HyperChem molecular modeling program, was applied based on Polak-Ribiere optimization algorithm, restricted Hartree-Fock wavefunction, the convergence limit of 0.0001 kcal/mol and RMS gradient of 0.0001 kcal/(Å mol).

CONCLUSIONS

From the McRae's theory describing universal interactions, based on the influence of the solvent macroscopic parameters ϵ (dielectric constant) and n (refractive index) the types of solute-solvent volume interactions were identified with correlations coefficients of about 0.93 for the near UV band and respectively 0.75 for the far UV band. From solvatochromic theory based on the solvent empirical parameters α (hydrogen bond donor acidity), β (hydrogen bond acceptor basicity) and π^* (solvent dipolarity/polarizability) the role of local interactions accompanying the volume ones was evidenced which led to correlations coefficients of about 0.95 (for the near UV band) and 0.93 (for the far UV band).

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