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Solvent influence on the photophysical properties of 4-methoxy-*N*-methyl-1,8-naphthalimide

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Abstract

4-Methoxy-*N*-methyl-1,8-naphthalimide (**1**) exhibits considerable solvatochromism and its UV–vis spectral properties have been studied in several polar/non-polar and protic/aprotic solvents, as well as in ethanol–water mixtures. The results reveal a strong influence of the solvent's polarity and its hydrogen-bond donor (HBD) capability on the photophysical properties of **1**. For binary ethanol/water mixtures, preferential solvation models describe the band shifts in the probe's visible absorption spectrum well, but they fail to describe the corresponding shifts of the emission maxima. Pseudolinear approximations between solvent composition and molecule's transition energies, E_T , can be used to study the composition of ethanol–water mixtures, simplifying the mathematical treatment for eventual analytical applications.
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Keywords: Naphthalimide; Solvatochromism and spectrophotometric probe; Ethanol–water mixtures

1. Introduction

Several properties of chemical systems depend on the nature of their solvent. The solvent not only affects reaction kinetics, but also influences the characteristics of the spectra of the solute molecules. In some cases more than in others, this phenomenon is manifested by solvent-induced differences in the electronic, vibrational and NMR spectra. This property is known, when talking about spectral effects, as solvatochromism or, in a more general way, as perichromism (*peri*: around) [1]. Many factors influence the spectral behavior of dissolved molecules, especially the solvent's polarity, its temperature [2] and its hydrogen-bond donor (HBD) or acceptor (HBA) capacity [3–11].

In the case of UV–vis spectroscopy, strong solvatochromic effects are generally observed for dipolar molecules exhibiting large variations in their dipole moment during electronic

transitions. These variations can differentially stabilize the ground and/or the excited state in polar and non-polar solvents. Hydrogen-bond formation also affects the molecular orbitals energy levels considerably, influencing the molecular energetics in a similar way. By convention, the solvatochromic effect is said to be negative if blue band shifts are observed (hypsochromic shifts) with increasing solvent polarity. Conversely, positive solvatochromism occurs when red band shifts (bathochromic shifts) are observed in these circumstances. Generally, if one considers Franck–Condon excited states, molecules exhibiting a larger permanent dipole moment in the excited state ($\alpha_e > \alpha_g$) display positive solvatochromism. The opposite is observed in cases when the permanent dipole moment is larger in the ground state [1].

Several attempts have been made in order to quantify and predict solvatochromic effects and most of the solvatochromic solvent polarity scales have been built using empirical solvent parameters. Based on comparisons between different solvents, Kamlet and Taft have built a scale of solvatochromic parameters to be used in linear solvation

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energy relationships (LSERs). This scale comprises several solvent parameters, such as their HBD acidity and HBA basicity (α and β parameters), which estimate the solvent's ability to donate an H-atom or an electron pair in a solvent-to-solute hydrogen bond. Another parameter, the π^* index, measures the solvent's dipolarity and polarizability and its ability to stabilize charges by dielectric effects [12–14]. Catalán et al. have also developed a “single parameter solvent dipolarity/polarizability (SPP) scale”, which uses the gas phase (SPP = 0.000) and DMSO (SPP = 1.000) as reference media to fix the scale [15,16].

It is well known that 1,8-naphthalimide derivatives are very sensitive to their surroundings and their electronic emission and absorption spectra are frequently affected by the nature of the solvent. What is generally observed in *N*-alkyl-1,8-naphthalimide photophysics is a decrease in the fluorescence quantum yield as the solvent's polarity and its HBD capability increase. This happens mainly because of the proximity between the n , π^* and π, π^* excited states, which controls the excited-state conversion from singlet to triplet manifold, thus explaining the response in fluorescence yields.

In addition, the presence of electron-donor/acceptor groups attached to the naphthalene moiety is also very important because these substituents can activate or deactivate emitting modes, affecting their emission spectra considerably.

The presence of electron-donating substituents can also increase the separation between the singlet (S1) and its closer triplet excited state, thus decreasing the intersystem crossing (ISC) and favoring the fluorescence deactivation channel. Furthermore, *N*-naphthalimides modified with electron-donating groups can also allow photo-induced electron-transfer processes, generating photochemical diads and they can be part of even larger systems exploring the electron-transfer phenomena, such as triads and tetrads [17–22].

Solvatochromic compounds can be used as analytical UV–vis spectrophotometric probes [3–11] and, eventually, for water quantification in binary solvent mixtures. We have chosen to study ethanol–water mixtures, since hydrated ethanol has been used as a natural car fuel in Brazil for more than 20 years, being an alternative to gasoline. Dishonest distributors adulterate such fuel by adding water to it in order to increase its volume, thus largely exceeding the legally allowed water content in automotive ethanol (max. water content = 6.8 ± 0.4 mass%). This excess water causes engine malfunctioning and accelerates the wearing off of ethanol engines. Besides adding extra water, some distributors also correct the mixture density by means of other impurities, making the densimeters useless for the control of water content in the fuel. In this case, solvatochromic spectrophotometric probes could become an alternative for fast certification analysis, since they are easier to use than the traditional Karl–Fischer titration method for precise water-content determinations and much cheaper than specific NIR

methods. This kind of probe could also be used in quality control in colorless liquor production, such as cachaça (a sugar-cane liquor and export product), vodka, rum and gin.

This paper presents some of the solvatochromic properties of 4-methoxy-*N*-methyl-1,8-naphthalimide (**1**) in several solvents and in ethanol–water binary mixtures, and shows how it could be used as a UV–vis spectrophotometric probe for analytical purposes.

2. Experimental

2.1. Synthesis of 4-methoxy-*N*-methyl-1,8-naphthalimide (**1**)

4-Methoxy-*N*-methyl-1,8-naphthalimide (**1**) (Fig. 1) was obtained from 4-nitro-*N*-methyl-1,8-naphthalimide, which was synthesized from 4-nitro-naphthalic anhydride and methylamine by a sonochemistry route [23].

4-Nitro-*N*-methyl-1,8-naphthalimide (1.0×10^{-3} mol) was dissolved with five equivalents of potassium carbonate in 35 mL of methanol and the solution was sonicated in an ultrasonic cleaner bath (Branson, 150 W/25 kHz output) in a 40 mm diameter cylindrical reaction vessel. The reaction was monitored by TLC [Merck silica gel plates with fluorescent indicator (254 nm), using CH_2Cl_2 as eluent]. At the end of the reaction, the solvent was removed in vacuo, the residue was dissolved in CHCl_3 and the solution was washed several times with 10% aqueous sodium hydroxide and water and dried in vacuum to give pale yellow needles (yield = 97%) of mp = 197–198 °C (in Ref. [24] mp = 197–201 °C). The melting point was measured in an electrothermal melting point apparatus. ^1H NMR spectra were recorded on a Bruker AC-200 (in CDCl_3). The IR spectrum was registered on a BOMEM-FTIR MB 102 spectrophotometer, in the range 300–4000 cm^{-1} , in KBr pellets. Capillary GC analysis was performed on a HP-5890 coupled to an MSD-5970 mass selective detector.

$R_f = 0.21$ (CH_2Cl_2); ^1H NMR (CDCl_3): $\delta = 3.5$ (s, 3H, CH_3), 4.0 (s, 3H, CH_3), 7.0 (d, $J = 8.2$ Hz, 1H, Ar), 7.6 (t, $J = 8.2$ Hz, 1H, Ar), 8.5 ppm (m, 3H, Ar); MS: (m/z) = 241 (M^+ , 100), 213, 198, 182, 113; IR (KBr): $\tilde{\nu} / \text{cm}^{-1} = 3021, 2945, 1698, 1658, 1580, 1356, 1254, 1077$; Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$: N, 5.81; C, 69.70; H, 4.60. Found: N, 5.86; C, 69.68; H, 4.63%.

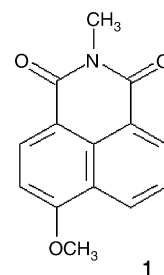


Fig. 1. 4-Methoxy-*N*-methyl-1,8-naphthalimide.

2.2. Measurements

UV–vis spectra were recorded on a Shimadzu UV-2401PC spectrophotometer at 25 °C. Emission data were obtained using a Photon Technology International LS1 spectrofluorimeter. All emission spectra were corrected as a function of the lamp intensity, using the equipment software. The absorption and emission maxima were calculated using the spectra first derivatives, at the point where they cross the x -axis. All solvents are of analytical grade.

3. Results and discussion

In order to study the solvatochromic properties of **1**, a mother solution was prepared from 2 mg of **1** in 50 mL ethanol ($c = 1.65 \times 10^{-4} \text{ mol L}^{-1}$), where it is fairly soluble. All the samples used in this work were prepared from starting portions of 1 mL of this solution. This amount was placed in a flask, ethanol was evaporated and 5 mL of solvent was added in order to obtain solutions of imide **1** with $c = 3.3 \times 10^{-5} \text{ mol L}^{-1}$. In this study, 14 different solvents were used in order to explore the solvatochromic effect in different media. In this concentration range, **1** was soluble in all solvents. Polar and non-polar solvents were employed, but all of them were non-aromatic, in order to eliminate π -type solvent–solute interactions. The chosen solvents present different hydrogen-bonding abilities and this was also taken into account in this work. By observing Figs. 2 and 3, one can easily notice that the solvent exerts a great influence on both the electronic absorption and emission spectra, changing their shape, spectral maxima positions and intensities. All the spectra can be assembled in basically three sets of spectral patterns. The first one occurs with all non-polar solvents, like isooctane; another is present in the case of all dipolar non-HDB solvents, like DMSO and a third pattern can be detected in hydrogen-bond donor solvents, like alcohols and water.

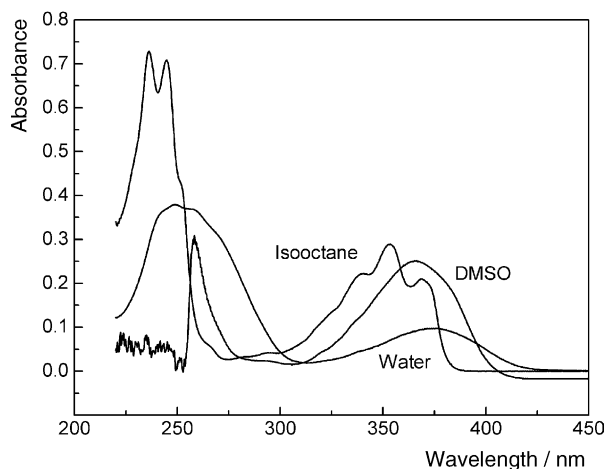


Fig. 2. UV–vis absorption spectra of $3.3 \times 10^{-5} \text{ mol L}^{-1}$ 4-methoxy-*N*-methyl-1,8-naphthalimide (**1**) solutions in three solvents of different polarity.

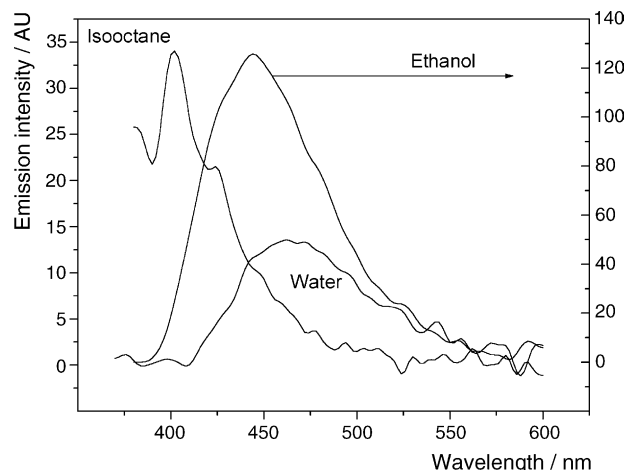


Fig. 3. UV–vis emission spectra of $3.3 \times 10^{-5} \text{ mol L}^{-1}$ 4-methoxy-1,8-*N*-methyl-naphthalimide solutions in three solvents ($\lambda_{\text{exc}} = \lambda_{\text{abs}}^{\text{max}}$ for each solvent: 353 nm for isooctane, 475 nm for water and 363 nm for ethanol).

In the visible region of the spectrum, the first solvent type generates well-resolved absorption spectra, showing vibronic bands separated by $\Delta\lambda \approx 15 \text{ nm}$, which correspond to the $\pi-\pi^*$ S^1 level transitions. The $n-\pi^*$ band is also visible, but weaker, around $\lambda_{\text{max}} = 294 \text{ nm}$. The second spectral type consists of spectra with a single band above $\lambda_{\text{max}} = 350 \text{ nm}$, with comparable intensities, but without fine structure. In HBD solvents (water, methanol, ethanol, 1-propanol, 2-butanol and 2-methyl-1-propanol, some not shown), a much less intense broadened band, without fine structure appears. These bands intensities are very close to each other in all solvents, except for water.

The emission spectra show basically the same behavior. Well-resolved bands are obtained in non-polar solvents, which are assigned to $S^0 \leftarrow S^1$ transitions. In polar solvents, the bands are broadened and collapsed, when compared with other solvents. In the case of HBD solvents, like water and alcohols, this effect is more pronounced than in the case of all other solvents. The solvent–solute hydrogen-bond formation is very clear in both absorption and emission spectra. Positive solvatochromic shifts are observed as a difference of $\Delta\tilde{\nu} = 1660 \text{ cm}^{-1}$ between absorption maxima ($\Delta\lambda_{\text{max}} = 22 \text{ nm}$ for water and isooctane) and of $\Delta\tilde{\nu} = 3230 \text{ cm}^{-1}$ between emission maxima ($\Delta\lambda_{\text{max}} = 60 \text{ nm}$ for water and isooctane), as one goes from a polar to a non-polar solvent, showing that the transition energy decreases with increasing solvent polarity. The spectral data are reported in Table 1.

Good linear correlations between Catalán's SPP parameter and absorption and emission maxima, as well as Stoke's shifts are obtained, as can be observed in Fig. 4. It is clear that in non-HBD solvents, the spectral data fit very well, correlation with SPP: $r = 0.996$ for Stokes shifts; $r = 0.963$ for absorption and $r = 0.994$ for emission energies, indicating that the observed solvatochromic effect is mainly due to dipolarity/polarizability interactions taking place when hydrogen bonds are not involved. This parameter is quite useful to

Table 1
UV–vis spectroscopic data for solutions of naphthalimide **1** in 11 solvents

Solvent	$\lambda_{\text{max}}^{\text{abs}}$ (nm) \pm 0.5 ($\tilde{\nu}$, cm^{-1})	ϵ (mol dm $^{-3}$ cm $^{-1}$)	$\lambda_{\text{max}}^{\text{em}}$ (nm) \pm 0.5 ($\tilde{\nu}$, cm^{-1})
H ₂ O	375 (26666)	2240	462 (21645)
MeCN	360 (27777)	9120	434 (23041)
MeOH	364 (27472)	8450	450 (22222)
EtOH	363 (27548)	8120	444 (22522)
Cyclohexane	355 (28169)	11330	404 (24752)
<i>n</i> -Dodecane	355 (28169)	8700	402 (24875)
THF	359 (27855)	8420	430 (23255)
DMSO	365 (27397)	7640	452 (22123)
DMF	363 (27548)	9550	444 (22522)
Isooctane	353 (28328)	8760	402 (24875)
CCl ₄	357 (28011)	9600	412 (24271)

[*c* (**1**) = 3.3×10^{-5} mol L $^{-1}$].

describe and predict the behavior of **1** in all non-HBD solvents. An increase in the SPP parameter causes a decrease in the transitions energies, as would be expected for a positive solvatochromism.

This kind of behavior has been observed by Barros et al. [22] with other naphthalimides and it can be assigned to the proximity between the n, π^* and π, π^* transition energies. Increasing medium polarity diminishes the π, π^* energy, increasing its contribution to the mixed n, π^* ; π, π^* state, leading to an enhanced π, π^* character in the LUMO energy.

On the other hand, the HBD solvents do not behave in this way, generating random values when compared to other solvents. The maxima for water, ethanol and methanol have also been plotted in Fig. 4 (the cross-marked shapes) and no correlation with these parameters is apparently possible, once the variations in absorption and emission data when one alcohol is substituted for another are not at all predictable. Data for 1-propanol, 2-methyl-1-propanol (isobutanol) and 2-butanol are very similar and are not shown. As can be seen, alcohols and water must be treated as a special case and this

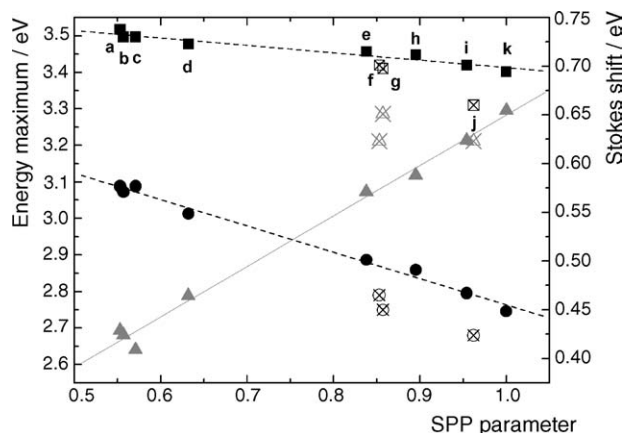


Fig. 4. Absorption (■) and emission (●) maxima and Stokes shifts (▲) of 3.3×10^{-5} mol L $^{-1}$ 4-methoxy-1,8-*N*-methyl-naphthalimide (**1**) solutions in different solvents: a, isooctane; b, cyclohexane; c, *n*-dodecane; d, tetrachloromethane; e, tetrahydrofuran; f, ethanol; g, methanol; h, acetonitrile; i, *N,N*-dimethylformamide; j, water; k, dimethyl sulfoxide.

has already been considered by Catalán et al., who had to create an additional acidity scale to explain solvatochromism in these solvents [16]. HBD solvents can easily form hydrogen bonds, binding to the molecule's carbonylic oxygens of the molecule and, possibly, to the methoxy group. The influence of this kind of interaction via carbonylic oxygens is very strong in the spectroscopic properties of the naphthalimide. This has been proven by Pardo et al., who have studied the influence of intramolecular hydrogen bonds formed by substitutes of the imidic nitrogen [25–27], as well as the protonation of the imidic substituents. All these elements seem to indicate that the origins of this different solvatochromic effect in HBD solvents lie in the specific solvent–solute interactions occurring mainly with the carbonylic oxygens.

Several attempts have been made to correlate these parameters with absorption and emission intensities. Once the experiments in all solvents have been carried out in the same conditions, we have tried to correlate the emission/absorption integrals ratio with the scale mentioned above, as if it was a relative quantum yield, but there is no reliable experimental relationship between values in this specific case (details in the supporting information). In addition, lifetimes and fluorescence quantum yields should increase with increasing SPP, as predicted in theory and verified by Pardo et al. [26], but this fact could not be experimentally verified in our case.

Theoretical calculations (see supporting information) were carried out in order to explain the stabilization of the excited state in polar solvents. The results in vacuum, however, do not reveal appreciable dipole moment variations during HOMO–LUMO transitions.

In order to study the behavior of **1** in ethanol–water mixtures, the same amount of this imide was dissolved in 11 numbered ethanol–water mixtures with growing ethanol content. This choice was made for commercial reasons, as explained in Section 1 of this paper. The absorption and emission maxima in these different binary solvent mixtures were measured and are reported in Table 2.

Fig. 5 shows the absorption maxima energy of **1** as a function of the composition of the binary mixtures (in %, v/v) and the molar fraction of water. Volumetric variations due to mixture contraction have not been taken into account, once they would affect the transitions intensities rather than their maxima. At a first glance, one can imagine that a linear correlation exists between absorption energy and the mole fraction of ethanol ($\chi(\text{ethanol})$ or χ_2). In order to simplify the equations, water will be called solvent 1 and ethanol will be solvent 2. χ_1 and χ_2 correspond to their respective mole fractions. A correlation factor of $r = 0.9935$ can be obtained from this data ($E_T = E_{\text{water}} + 0.098(\pm 0.003)^* \chi_2$). However, the emission maxima (Fig. 6) clearly show that this is not necessarily the case. The emission data describe an exponential function instead of a straight line. In fact, experimental data fit quite well into the function $E_{\text{emission}} = E_{\text{water}}^{\text{emis}} + e^{(\chi_2/(-t))}$ with $t = 0.22$ ($r = 0.99$). The pseudolinear approach, using a single line, is only valid for absorption maxima, where differences in energy are smaller.

Table 2

UV–vis spectroscopic data for naphthalimide (**1**) solutions in eleven ethanol–water mixtures

Mixture (% ethanol, v/v)	Water mole fraction χ water	$E_{\text{abs}}^{\text{max}}$ (eV) ($\pm 6.8 \cdot 10^{-3}$) (λ_{max} , nm; $\tilde{\nu}$, cm^{-1})	$E_{\text{abs}}^{\text{max}}$ (eV) ($\pm 6.8 \cdot 10^{-3}$) (λ_{max} , nm; $\tilde{\nu}$, cm^{-1})
0 (0%)	1	3.310 (375; 26673)	2.696 (460; 21720)
1 (10%)	0.966	3.312 (375; 26688)	2.707 (458; 21815)
2 (20%)	0.927	3.317 (374; 26709)	2.729 (455; 21992)
3 (30%)	0.882	3.319 (374; 26745)	2.749 (451.5; 22148)
4 (40%)	0.827	3.330 (373; 26838)	2.579 (450; 22232)
5 (50%)	0.762	3.339 (372; 26910)	2.790 (445; 22482)
6 (60%)	0.681	3.350 (370.5; 26990)	2.797 (444; 22537)
7 (70%)	0.578	3.357 (370; 27048)	2.805 (442.5; 22598)
8 (80%)	0.445	3.366 (369; 27122)	2.812 (441; 22655)
9 (90%)	0.262	3.379 (367; 27233)	2.821 (440; 22727)
10 (100%)	0	3.410 (364; 27480)	2.831 (438; 22810)

[c (**1**) = $3.3 \times 10^{-5} \text{ mol L}^{-1}$].

In order to use a linear approximation with emission data, it is necessary to use two lines instead of one. The first linear equation ($E^{\text{emission}} = E_{\text{water}}^{\text{emis}} + 0.393(\pm 0.023) \cdot \chi_2$; $r = 0.992$) would describe the emission energies for mixtures with low ethanol content ($\chi_2 < 0.24$) and the second ($E^{\text{emission}} = E_{\chi_2=0.24}^{\text{emis}} + 0.052(\pm 0.003) \cdot \chi_2$; $r = 0.989$) for mixtures with higher ethanol content ($\chi_2 > 0.24$).

As there are small shifts in the absorption energies, this pseudolinearity can be used for analytical purposes in composition-maxima correlations when absorption spectra are concerned. The stars plotted in Fig. 5 are real samples: one consists of automotive ethanol, the other is cachaça. It is obvious that two samples are not enough to establish any analytical chemistry statement, but they are enough to show that a correlation is possible. According to their absorption maximum (obtained from the 0 value of the first derived), the gas station automotive alcohol contains 96 vol.% ethanol, while

cachaça contains 46 vol.%, which corresponds to 46 °GL (degrees Gay–Lussac). The nominal value for both is 96% and 50 °GL, respectively. However, this is a simplification and these plots should formally be considered as polynomial functions, which is common for other solvent mixtures [28,29].

Several models have been created to explain solvatochromism in solvent mixtures and one of the most employed nowadays is the preferential solvation model [30–35]. This model assumes that, in a mixture of solvents, the one with greater affinity for the solute will preferentially compose the solvation microsphere. This kind of approach has been well described in several papers [34,35] and the mathematical treatment of the experimental data becomes gradually more complicated as more realistic models of the solvation phenomenon are considered. Simple correlations between the composition of solvent mixtures and solute absorption maxima are only obtainable when the two solvents do not interact between themselves strongly, i.e. when

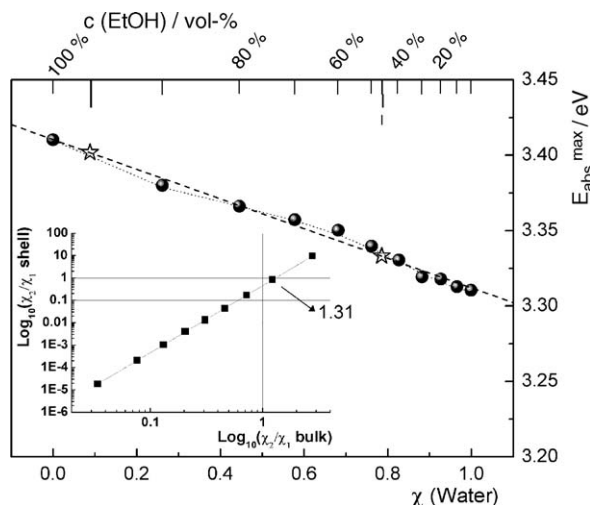


Fig. 5. UV–vis absorption maxima of 4-methoxy-1,8-*N*-methyl-naphthalimide solutions in ethanol–water mixtures, as a function of their composition [c (**1**) = $3.3 \times 10^{-5} \text{ mol dm}^{-3}$]. The two stars represent real samples, the first one is automotive ethanol and the second one is cachaça (at 96 and 48%, respectively). The dashed line corresponds to the adjusted curve. Inset: plot of solvent composition in the bulk and in the solvation sphere (solvent 2 is ethanol, see text below).

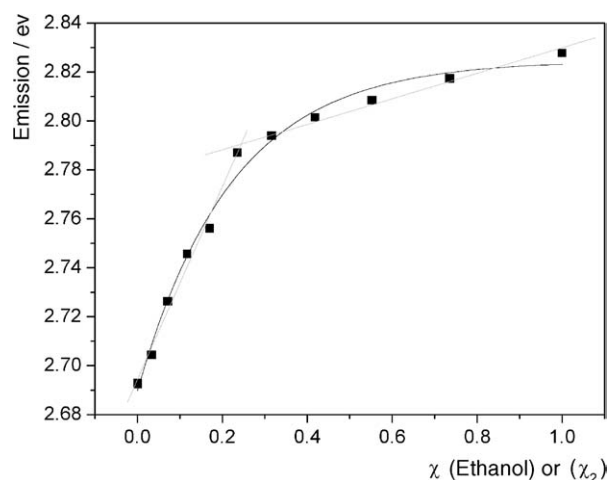
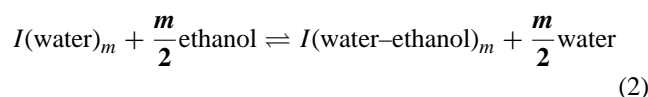
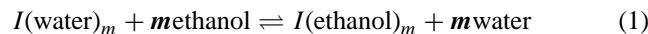


Fig. 6. Emission maxima of 4-methoxy-1,8-*N*-methyl-naphthalimide solutions in ethanol–water mixtures ($\lambda_{\text{exc}} = 370 \text{ nm}$, [$3.3 \times 10^{-5} \text{ mol dm}^{-3}$]) as a function of the ethanol mole fraction of the mixture and the exponential function adjusted to experimental data. In gray: linear regressions for data in two intervals: $\chi_2 < 0.24$ and $\chi_2 > 0.24$.

no synergetic effect is observed. In our case, ethanol and water do interact very strongly [36,37] (type 2 solvents, according to the classification of Rosés et al.), but they do not seem to form the so-called “highly polar hydrogen-bond complexes” [34] responsible for synergetic effects in the spectra of binary mixtures. However, these solvents behavior cannot be explained with simpler models. To describe this system using the models presented by Rosés et al. or by Skwierczynski and Connors, we have to use the m model which is the most complex. However, it seems to be the only model that provides good correlation with experimental data.

The m model assumes that equilibria occur between the solvents that compose the solvation microsphere of a solvatochromic indicator in binary solvent mixtures and these solvents can be exchanged. The solvatochromic indicator can be solvated by m molecules of water, ethanol or both. The equilibria between the solvated forms Eqs. (1) and (2) depend on the affinity of the solvents for the solute, on the interactions between them and on the composition of the mixtures. These equilibria are shown in Eqs. (1) and (2).



The constants for these processes are defined by:

$$f_{2/1} = \frac{\chi_2^{\text{sphere}} / \chi_1^{\text{sphere}}}{(\chi_2^{\text{bulk}} / \chi_1^{\text{bulk}})^m} \quad (3)$$

$$f_{12/1} = \frac{\chi_{12}^{\text{sphere}} / \chi_1^{\text{sphere}}}{\sqrt{(\chi_2^{\text{bulk}} / \chi_1^{\text{bulk}})^m}} \quad (4)$$

where χ 's represent the molar fractions of solvents 1, 2 and co-solvent 12, in both the bulk and solvation microsphere. f constants (Eqs. (3) and (4)) measure if the solute is best solvated by solvent 2 instead of 1 ($f_{2/1}$) or by a mixture of them ($f_{12/1}$). The normalized transition energies vary as a function of these parameters and of the molar fraction of solvent 2 (χ_2^{bulk}), according to expression (5).

$$E_T^N = 1 - \frac{a(\chi_2^{\text{bulk}})^m + c\sqrt{[(1 - \chi_2^{\text{bulk}})\chi_2^{\text{bulk}}]^m}}{(1 - \chi_2^{\text{bulk}})^m + f_{2/1}(\chi_2^{\text{bulk}})^m + f_{12/1}\sqrt{[(1 - \chi_2^{\text{bulk}})\chi_2^{\text{bulk}}]^m}} \quad (5)$$

Coefficients a and c depend on $f_{1/2}$ and $f_{12/1}$, as shown in expressions (6)–(8). Term c provides the value of $E_{\text{Twater-ethanol}}^N$, which is the transition energy of the transition in a solvation microsphere containing both solvents.

$$a = f_{2/1}(E_{\text{T-ethanol}}^N - E_{\text{T-water}}^N) \quad (6)$$

$$(E_{\text{T-ethanol}}^N - E_{\text{T-water}}^N) = 1 \quad (7)$$

$$c = f_{12/1}(E_{\text{T-water-ethanol}}^N - E_{\text{T-water}}^N) \quad (8)$$

In this general model, m is the number of solvent molecules in the solvation microsphere of the solvatochromic indicator affecting its transition energies.

Adjustment of the experimental data by non-linear regression with the aid of the Levenberg-Marquardt algorithm (dashed line, Fig. 5) leads to the $E_{\text{Twater-ethanol}}^N$, $f_{2/1}$ and $f_{12/1}$ parameters, respectively, corresponding to $0.59 (\pm 5.10^{-2})$, $0.43 (\pm 0.24)$ and $5.05 (\pm 0.77)$ for $m = 3$ solvent molecules in the solvation microsphere. According to these numbers and to the m preferential solvation model, the solvation microsphere should be mainly composed of water molecules throughout almost all the composition range of the mixture. In other words, the imide should be poorly solvated by ethanol. We should always remember that this model is oversimplified [38] and the m number may not be enough to describe the whole solvation microsphere.

However, emission data cannot be fitted to equations similar to Eq. (5), when values of $m = 3$ and $f_{2/1} = 0.43$ are used and when it is admitted that the solvation sphere does not change during the electronic transition, as should be the case of a Franck–Condon transition. These parameters should be maintained, unless the lifetime of the excited state of **1** is long enough ($>10^{-10}$ s) to allow configuration relaxation of the solvation microsphere which seems to be the case.

4. Conclusion

The UV–vis absorption and emission spectra intensity, shape and energy of **1** are strongly solvent-dependent, as it is the case of some of its analogs [16–18]. The absorption maxima exhibit linear behavior, in agreement with Catalán's SPP parameter, as well as with Kamlet–Taft's π^* parameter. The exception are HBD solvents such as water and alcohols, which cause different effects on the spectra. Solvents forming hydrogen bonds generate significant deviations from these correlations and they should be treated separately. In these cases, the full Kamlet–Taft model should be used, including π^* , α and β parameters.

The positive solvatochromic effect suggests that stabilization of the excited states occurs in polar solvents. However, the semi-empirical calculations in vacuum were not able to give evidence of great variations in dipole moments during the electronic transition, which could justify this observation.

The more efficient solvatochromic probes are generally complex, charged, conjugated molecules that are frequently unstable or insoluble in some kind of solvent. In spite of displaying relatively small solvatochromic shifts, imide **1**, is a very simple, small and stable molecule that can be synthesized in large amounts by the sonochemical route. Also, it is soluble in most solvents, at least sparingly. This imide can be employed as a cheap solvatochromic probe in ethanol–water mixtures, using the absorption or emission maxima pseudo-linear approximation. This is especially useful for automotive ethanol and liquor industry quality control. In mixed solvents, the chromophore can be viewed as the center of a cavity,

surrounded by hydrogen-bond forming molecules. When two solvents coexist, competitive solvation occurs at different degrees, according to their proportions and these two solvents take part in the composition of the solvation cavity. In the case of ethanol and water, the solvents interact with each other, forming solvent–solvent hydrogen bonds, which change the bulk structure of the pure solvents. This reflects in the composition of such cavity. These changes should also modify the availability of water binding hydrogens, gradually changing the spectrum of **1**. The preferential solvation models have shown that **1** is best solvated by water and changes in the solvation sphere occur during decay of its excited state.

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Appendix A. Supplementary data

Supplementary data have been deposited with the British Library at Boston Spa, Wetherby, West Yorks, UK as Supplementary Publication No. SUP... (... pages). Persons wishing to obtain copies of the deposited material should contact Service Enquiries, British Lending Library, Boston Spa, Wetherby, West Yorks LS23 7BQ, UK citing the SUP number. Tel.: +44 1937 546 060; fax: +44 1937 546 333; e-mail: dsc-sutomer-services@bl.uk.

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