

The Negative Solvatochromism of Reichardt's Dye B30 – A Complementary Study

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The UV/Vis spectra of a hypothetical negative solvatochromic dye in a solvent are theoretically calculated assuming the classical damped harmonic oscillator model and the Lorentz-Lorenz relation. For the simulations, the oscillator strength of the solvent was varied, while for the solute all oscillator parameters were kept constant. As a result, a simple change of the oscillator strength of the solute can explain the redshift and intensity increase of the UV/Vis band of the solute. Simulated results are compared with measured UV/Vis spectroscopic data of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate **B30**

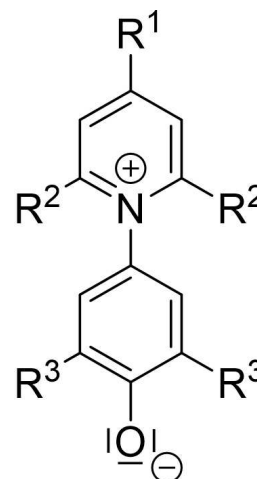
(Reichardt's dye). Significant correlations of the absorption energy ($1/\lambda_{\text{max}}$) with the molar absorption coefficient ϵ as function of solvent polarity are demonstrated for several derivatives of **B30**. The approach presented is only applicable to negative solvatochromism. Therefore, while the approach is vital to fully understand solvatochromism, it needs to be complemented by other approaches, e.g., to describe the changes of the chemical interactions based on the nature of the solvent, to explain all its various aspects.

Introduction

Reichardt's dye **B30**, 2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Scheme 1) has been established as one of the most important probe molecules for determining solvent properties by means of UV/Vis spectroscopy during the last four decades.^[1–9] The reason for declaring the molar transition energy of the **B30** dye as an empirical polarity scale ($E_{\text{T}}(30)$ parameter) was the fact that results of many solvent-dependent processes could apparently be explained with it.^[1–9]

The original $E_{\text{T}}(30)$ parameter is defined as the molar absorption energy of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (**B30**, see scheme 1) (eq. 1) at the UV/Vis peak maximum (λ_{max}) measured in a certain solvent.^[2,3,4]

$$E_{\text{T}}(30)(\text{kcal mol}^{-1}) = 28591/\lambda_{\text{max}}(\text{B30}) \quad (1)$$



Scheme 1. Solvatochromic dyes of the Reichardt type: 4-(2,4,6-triphenylpyridinium-1-yl) phenolate (**B1**), 2,6-di-*tert.* butyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (**B26**), 2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (**B30**). **B30**: $R^1 = R^2 = R^3 = -\text{C}_6\text{H}_5$; dye **B1**: $R^1 = R^2 = -\text{C}_6\text{H}_5$, $R^3 = \text{H}$; dye **B26**: $R^1 = R^2 = -\text{C}_6\text{H}_5$, $R^3 = -\text{C}(\text{CH}_3)_3$. The numbering of the dyes is in accord to Ref. [7].

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cphc.202200100>

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The spectral footprint of the electronic transition of **B30** as function of solvent property has been subject of numerous experimental and theoretical studies in literature.^[10–26] Due to the electronic ground state being more polar than the first exciting state, strong dipole/dipole interactions of the dye with the solvent in the ground state should determine the UV/Vis absorption property and lead to significant negative solvatochromism.^[11–15] This is, nowadays, the classic teaching.^[1,2]

Nevertheless, there are still doubts about the correct physical interpretation of the $E_{\text{T}}(30)$ parameter.^[10–26] Since dipolar influences of the solvent in terms of the static dielectric constant (ϵ_s) play an essential role with respect to the dielectric function via the Clausius-Mossotti relation $f(\epsilon_s) = (\epsilon_s - 1)/(2\epsilon_s +$

2),^[5,18] the different effects of hydrogen bond donating (HBD) compared to non-HBD solvents were already recognized in the first work on this topic.^[7] For both solvent families, separate logarithm-like curves of $E_r(30)$ against the dielectric constant $f(\epsilon_r)$ are found.^[7] It should be noted that secondary and tertiary alcohols are located exactly between two solvent groups, primary alcohols and aprotic ones, in the diagram.

Historically, changes of the color of dyes in solvents have been investigated systematically already in the midst of the 19th century.^[27–30] Kundt formulated a rule in 1871 according to which the absorption of the dye is shifted towards the red the stronger the dispersion of the solvent in this spectral range is.^[29] Kundt's rule was discussed at length in volume 3 of Kayser's famous Handbook of Spectroscopy which appeared 1905.^[30] The nearly unanimous opinion at that time was that Kundt's rule cannot be applied if "chemical influences are evident", but the physical fundament of Kundt's rule could not be revealed.

In fact, as has been shown recently, it is the influence of the ordinary non-linear effect of polarization of matter by light (the effect is non-linear in the sense that the linear approximation according to Beer's law does no longer hold), in the simplest case described by the Lorentz-Lorenz relation, that causes the redshift and the intensity changes.^[31–33] Certainly, in many cases, additional chemical interactions will cause changes in both the transition dipole moment and the distance between HOMO and LUMO, but the polarization effect will most certainly always be in play and has to be considered together with the chemical interactions.

It is unsatisfactory that intensity changes in the UV/Vis-spectrum of a dye depending on the nature of the solvent have so far not been accepted as a criterion for the evaluation of solvent influences.^[1a] One reason for the nonacceptance is that the molar absorption coefficient ϵ of normal dyes, for example like crystal violet,^[34] substituted 5-methylisoindolo [2,1-a] quinolines^[35] or azobenzens,^[36] is practically not influenced by the type of solvent. It is hard to find reasonable correlations of ϵ with any empirical or physically determined polarity parameter of the solvent.^[1,34–39] For example, ϵ clearly increases from 16 000 Lmol⁻¹cm⁻¹ to 20 000 Lmol⁻¹cm⁻¹ for the positive solvatochromic dye 4-nitroaniline with increasing solvent polarity going from 1,4-dioxane, propylene carbonate to DMSO.^[37] However, in water a lower ϵ about 14 000 Lmol⁻¹cm⁻¹ is again found.^[38] Furthermore, for the positive solvatochromic dye 4-*N,N*-dimethylamino-4'-nitrostilbene, (**DANS**), no correlation of ϵ with the polarity of the solvent is recognizable,^[39] despite the dramatical increase in dipole moment on optical excitation of **DANS**.^[1b] Therefore, it was concluded: "solvent effects on the intensity of UV/Vis absorption bands cannot be interpreted in a simple qualitative fashion".^[1a]

These discouraging results for positive solvatochromic dyes led to the decision not to consider the influence of the polarity of the solvent on the intensity of the UV/Vis absorption (peak maximum), although such results were reported for the dye **B30** and were also confirmed by older and further work.^[7,40–42]

Liptay discussed as early as 1965 that the dye **B26** (Scheme 1) exhibits a strong negative solvatochromism associated with a drastic change in intensity, but a full interpretation

was not given despite sophisticated theoretical analysis of the subject.^[40]

Recently, relationships between Beer's law and the Clausius-Mossotti/Lorentz-Lorenz equation, respectively, were recognized.^[31–33] This actual finding shows the physical resilience to test correlations of UV/vis-spectroscopic energy and concentration resp. volume data of solvents considering ignored ϵ data from literature.^[7]

In this work we will consider results of three derivatives of **B30** from Ref. [7] as shown in Scheme 1. The 6 to 7fold increase of ϵ of **B30** and **B26** going from methanol to 1,4-dioxane resp. benzene is worth of a profound discussion.

We want to show that for negative solvatochromism another physical relationship due to the polarization of matter by light plays the major role in contrast to positive solvatochromism which has apparently led to this false equal evaluation of ϵ as function of solvent polarity.

Results and Discussion

Fundamental to the following discussion is that we assume a solvent that acts only as a dielectric background, very much as this was done by Bayliss.^[43] If the variance of chemical interactions plays a larger role, or if the solute is chemically altered by interaction or complexation in the solvent, the effect introduced by the polarization of matter by light that we discuss in the following is still at work, but will be superimposed by intensity changes and spectral shifts introduced by the chemical modifications, which certainly can dominate. Such effects will be explicitly excluded in the following.

From the point of view of the Lorentz-Lorenz relation, a relationship between ϵ and $\tilde{\nu}_{\max}$ can be established. This relationship is a consequence of the polarization of matter by light on which the Lorentz-Lorenz relation is based.^[44] The induction of dipole moments caused by the displacements of electrons counteract their cause. The effects are in particular large at and around absorptions. If we use the classical model of dispersion theory, we can model an UV/Vis-absorption with a damped harmonic oscillator. Without the interaction with light, damped harmonic oscillators with different eigenfrequencies do not interact, but when they are light-driven, they become coupled. The coupled oscillators have changed eigenfrequencies and oscillator strengths which are a function of the coupling strength. This light-mediated interaction is a function of spectral and locational distance of the oscillators, but there is no difference if those are located on the same or a different kind of molecule. This means that the oscillators of a different kind of molecules in a solution couple in the same way as those of chemically identical molecules in a neat substance. Historically, the first relation that was able to treat the effect for neat substances as well as for homogeneous mixtures of gases, liquids or solids was the Lorentz-Lorenz relation.^[44]

According to Lorentz-Lorenz, the square of the complex index of refraction $\hat{n}^2(\tilde{\nu})$ is given by eqn. 2.^[31]

$$\hat{n}^2(\tilde{\nu}) = 1 + \frac{N \cdot \hat{\alpha}(\tilde{\nu})}{\varepsilon_0 - \frac{1}{3}N \cdot \hat{\alpha}(\tilde{\nu})} = \frac{1 + \frac{2N \cdot \hat{\alpha}(\tilde{\nu})}{3 \varepsilon_0}}{1 - \frac{1}{3} \frac{N \cdot \hat{\alpha}(\tilde{\nu})}{\varepsilon_0}} \quad (2)$$

Here, $\hat{n}_i(\tilde{\nu})$ represents the complex index of refraction of the mixture and $\hat{\alpha}(\tilde{\nu})$ the polarizability.^[30] N is the number of oscillators per unit volume which is linked to the molar concentration c by $N = c \cdot N_A$, where N_A is Avogadro's constant and ε_0 is the vacuum permittivity. Note that for diluted gases in the absence of the polarization effect holds $\hat{n}^2(\tilde{\nu}) = 1 + N \cdot \hat{\alpha}(\tilde{\nu})/\varepsilon_0$. This is still not on the level of today's backwards prevalent theory, which assumes that $\hat{n}(\tilde{\nu}) = 1 + N \cdot \hat{\alpha}(\tilde{\nu})/(2\varepsilon_0)$ which leads to the use of Lorentz-profiles for absorption bands.^[44] In addition, effects due to permanent dipole moments are not considered, since any reorientation would be much too slow to be induced by light in the UV/Vis spectral region.

The idea behind the Lorentz-Lorenz relation is that under the effect of electromagnetic radiation matter is being polarized. The induced dipole moments change the local electric fields so that they are no longer equal to the applied electric field. In this sense, light changes the state of matter and this effect manifests itself by band shifts and intensity changes in spectra. In other words, the object of observation is changed by this observation, very much like the change of the momentum of an electron by the collision with a photon which manifests itself in the uncertainty principle, except that for simple cases the change due to observation can be corrected. In this sense, intensities and peak positions in spectra do not reflect eigenfrequencies and oscillator strengths in general. Lorentz and also another Nobel laureate, Max Planck, were well aware of this and included the effect of polarization explicitly into their approaches for describing the dispersion of light^[44,45] Based on dispersion theory, Planck could show that for a single damped harmonic oscillator the maximum of absorption is redshifted relative to the oscillator position.^[45] Note that Planck already explicitly described in his work the relation between oscillator strength and redshift, something which was nearly 50 years later rediscovered by Bayliss.^[43] Bayliss introduced an effect due to the solvent only through the (constant) refractive index of the solvent, which means that the coupling of oscillators of solute and solvent could not be accounted for. For systems of more than one oscillator, the coupling effect is usually not included into the damped harmonic oscillator model. Instead, the product of polarizability and number of oscillators per unit volume N in eqn. (2) is described by:

$$N\hat{\alpha}(\tilde{\nu}) = \sum_j c_j \sum_i \frac{S_{ji}^{*2}}{\tilde{\nu}_{0ji}^2 - \tilde{\nu}^2 - i\tilde{\nu}\gamma_{ji}} \quad (3)$$

In eqn. (3), S_{ji}^{*} is the molar oscillator strength of the i th oscillator of component j , $\tilde{\nu}_{0ji}$ the oscillator position and γ_{ji} its damping constant (in our simplified example, we assume two components, i.e., $j=1,2$ each with one oscillator so that $i=1$; note that according to eqn. (3) the polarizability of a mixture is

linearly dependent on the individual components. The coupling is introduced merely by the Lorentz-Lorenz relation and leads to differing apparent oscillator strengths and positions). The expression for $N\hat{\alpha}(\tilde{\nu})$ is then put into eqn. (3).

The oscillator strength as it is introduced here is based on classical dispersion theory and is historically a collective property, as the structure of matter was not known at the times it was developed, in contrast to its definition in quantum mechanics, where oscillator strength is connected with individual molecules.

In order to illustrate what eqn. (2) in combination with eqn. (3) predicts for different solvents, we have assumed for simplification that a solvent has only a single oscillator in the UV-Vis part of the spectrum at $\tilde{\nu}_{0,11} = 50000 \text{ cm}^{-1}$ with a damping constant $\gamma_{11} = 2000 \text{ cm}^{-1}$. Both quantities are fixed and we only vary the oscillator strength. For the solute, we assume a transition in the visible part of the spectrum at $\tilde{\nu}_{0,21} = 20000 \text{ cm}^{-1}$, also with a damping constant $\gamma_{21} = 2000 \text{ cm}^{-1}$, but, in contrast to Bayliss assumption,^[43] with a fixed molar oscillator strength $S_{21}^{*} = 15000 \text{ cm}^{-1}$. The volume fraction of the solute shall be 1%. If we now vary the molar oscillator strength S_{11}^{*} of the solvent from 3000 to 7000 $\text{cm}^{-1} \text{ mol}^{-1/2}$, eqs. (2) and (3) predicts the spectra depicted in Figure 1 (according to eqn. (3), the results would be the unchanged for different concentrations as long as the product of concentration and squared oscillator strength stays constant). Note that our assumptions lead to n_D^{20} values between 1.1 ($S_{11}^{*} = 3000 \text{ cm}^{-1} \text{ mol}^{-1/2}$) and 1.75 ($S_{11}^{*} = 7000 \text{ cm}^{-1} \text{ mol}^{-1/2}$), cf. Figure S16, a range which is slightly larger as the one that is covered by transparent organic solvents.

With increasing oscillator strength of the solvent, the peak shifts to the red, while the oscillator position and thus the difference between HOMO and LUMO remain constant (only the apparent oscillator strengths change, cf. Table S5).

As is known from the literature,^[46,47] eqs. (2) and (3) lead to an electromagnetic coupling of the oscillators. In this case it concerns the coupling between the solute and the solvent. The equations can also be used to model the dispersion of the

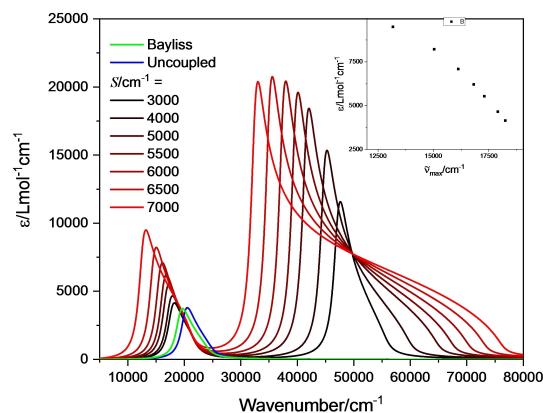


Figure 1. UV/Vis-Spectra of a hypothetical dye in different solvents characterized by having one oscillator at the same position and with the same damping constants but with different oscillator strengths. The inset shows the dependence of ε on the position of the peak maximum of the dye.

refractive index of the mixture $\tilde{n}^2(\tilde{\nu})$, with the obvious result (cf. Figure 1), that the positions of the oscillators would be red-shifted and the stronger band would feed the weaker. In other words, the seeming oscillator strength of the weaker band would be increased, whereas that of the stronger band would seem to be decreased. The reason is that the extra field provided by the surrounding molecules always increase the applied electric field, and, thereby, the Lorentz-Lorenz force, relative to that for an isolated molecule. This also means that this approach can only explain a redshift, which is the stronger the larger the oscillator strengths of the coupled oscillator(s) is. The latter leads to an increased refractive index and a stronger dispersion. This redshift corresponds to negative solvatochromism according to the definition. In case of positive solvatochromism additional influences like changing chemical interactions or complexations must be at play and be dominant. In general, electromagnetic coupling may be an important and even dominant mechanism, but for a full explanation of solvatochromism a unified model needs to be developed.

Note that to theoretically calculate the UV/Vis spectra in Figure 1 we just changed the oscillator strength S of the oscillator of the solvent, the square of which is proportional to the molar concentration of the absorbing species according to $S^2 = cS^*$ (please note also that because of this equation, Figure 1 does not change for different combinations of molar concentration and molar oscillator strengths as long as cS^* stays the same, cf. also the supporting information, section about apparent oscillator strengths and positions). In real settings, solvents certainly have more than one oscillator at different positions and strengths. But usually, the dispersion of transparent materials in the visible region can be described well with a single oscillator.^[28] The same should therefore be true with the effect of light polarization on solutes in transparent solvents. According to Figure 1, the relation between the position of the peak maximum and its value is approximately linear for lower oscillator strengths, but the intensity becomes saturated the more the peak of the solvent approaches the oscillator position of the dye. In practice, deviations can be expected for most solvent-solute combinations, since the Lorentz-Lorenz relation is based on a number of approximations like the assumption of spherical solvent and solute molecules and spherical coordination spheres around them, which restrict its quantitative applicability.^[33]

We have also added a spectrum to Figure 1 calculated according to Bayliss' model.^[43] This model disregards the coupling between oscillators and treats the influence of solvents only by the dielectric constant at optical frequencies, which describes the weakening of the light electric field by the solvent. Accordingly, any changes of $\tilde{\nu}_{\max}$ need to be introduced by changes of the oscillator strengths/transition moments. Certainly, chemical interactions can alter these, but it looks like that the simplification underlying Bayliss model, which was actually introduced much earlier already by Donnan,^[48] has so strongly influenced the corresponding literature, that in contemporary literature the strong effect through the coupling of the oscillators is completely disregarded (on a side note, the coupling is certainly mutual, which means that concentration

increases of the dye also lead to changes in the solvent part of the spectrum, see Ref. [32]).

As Figure 1 shows, the Lorentz-Lorenz relation is able to predict the order of the effects of solvent polarity on both position and intensity of solvent dependent UV/Vis spectra of a negative solvatochromic dye. The theoretical consideration of Figure 1 is strongly supported by the fact that ϵ (at peak maximum λ_{\max}) for **B30** strictly decreases with increasing solvent polarity, expressed as $1/\lambda_{\max}$ (eq. (1)), as demonstrated in Figure 2 and eq. 4. UV/Vis data are taken from Ref. [7]. For better compatibility with ϵ , we have used the UV/Vis peak position given in cm^{-1} for the diagram and correlations.

$$\epsilon(\tilde{\nu}_{\max})(\mathbf{B30})(\text{all solvents}) = -1161.4 \cdot \tilde{\nu}_{\max} 10^{-3} + 24572 \quad (4)$$

$$R^2 = 0.826 \quad (r = 0.918), n = 36$$

The simulated UV/Vis spectra of Figure 1 agree qualitatively well with the measured UV/Vis spectra of **B30** in ethanol, acetonitrile and 1,4-dioxane in the range of 10000 to 40000 cm^{-1} .^[16,3]

Until now, the following fixed rule was used when evaluating intensity data from UV/Vis spectra: these epsilon (at λ_{\max}) values are not a quantitative measure of the oscillator strength (classically S^2 or quantum mechanically f) or the total intensity of a UV/Vis absorption - only the area under a band, which is difficult to determine.^[49] In fact, the correctness of this statement depends on the oscillator strength of the UV/Vis-absorption band in question. A weak oscillator shows a Lorentzian shape in an absorbance spectrum and conforms to Beer's approximation. Since oscillator strength is proportional to the concentration, for such a band either each point at an arbitrary wavenumber or the intensity can be used, at least if coupling can be disregarded.^[50] Stronger damped harmonic oscillators become asymmetric and therefore only the integrated band area can be used,^[50] but only if coupling is absent. As can be seen in Figure 1, as soon as coupling has to be taken into account, not even the band area is a measure of the true

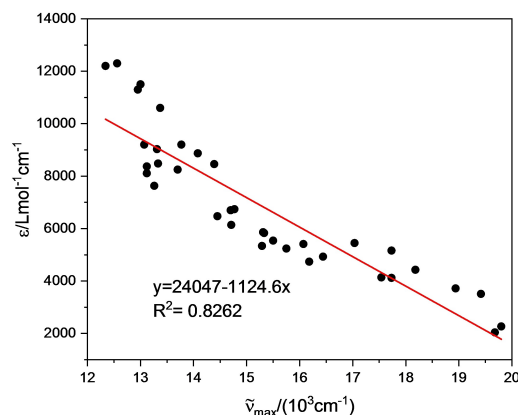


Figure 2. Correlation of the molar absorption coefficient at the UV/Vis peak maximum $\epsilon(\tilde{\nu}_{\max})$ as function of the absorption energy ($\tilde{\nu}_{\max}$ in cm^{-1}) of **B30** measured in a series of 31 organic solvents. Data used are compiled in Tab. S1 ESI part.

oscillator strength since the solute borrows an a priori unknown amount of oscillator strength from the solvent.

The longest wavelength CT absorption band of **B30** is not completely symmetrical and overlaps somewhat with shorter wavelength bands, so that the exact determination of the integral absorption intensity of **B30** would be difficult even if there would be no coupling with the solvent.

Nevertheless, the approximations introduced to derive the Lorentz-Lorenz relation must be kept in mind when the figures are interpreted, which are the assumption of a spherical molecule with a scalar polarizability in a spherical continuum built by the solvent molecules. Any chemical interactions which would change the function of the polarizabilities in dependence on the wavenumber of either solute or solvent are excluded since the calculation uses the oscillator parameters of the pure solute and the pure solvent.

Based on Figure 1, it seems that the blueshift and the intensity decrease of the E_T -30 peak shown in Figure 2 can be explained by a decrease of the overall oscillator strength of the solvent and/or a shift of the eigenfrequencies of the oscillators of the solvent to higher wavenumbers. It is assumed that this decrease in oscillator strength is due to a decreasing density/concentration of or a change of the main chromophore. This can be indirectly recognized, e.g., by a decrease in the refractive index at the Na-D line, e.g., from 1-butanol to ethanol and methanol and a decline of dispersion. In the same direction a blue shift occurs not only for **B30**, but also for **B1** and **B26** (Figure 3). In the case of the alcohols, the main chromophore are the C-H groups and the corresponding $\sigma \rightarrow \sigma^*$ transitions in the far UV.^[51] These transitions lose oscillator strength from 1-butanol to methanol because of the decreasing number of C-H groups per molecule.^[51] Correspondingly, the band due to $n \rightarrow \sigma^*$ blueshifts due to the decrease of oscillator strength of the $\sigma \rightarrow \sigma^*$ transitions (all oscillators of both solvent and solute are certainly also internally coupled according to eqn. (3)).

As Figure 3 shows, the blueshift of $\tilde{\nu}_{max}$ is also associated with a decrease of $\epsilon(\tilde{\nu}_{max})$ for **B26**, while this correlation is less well-pronounced for **B1**.

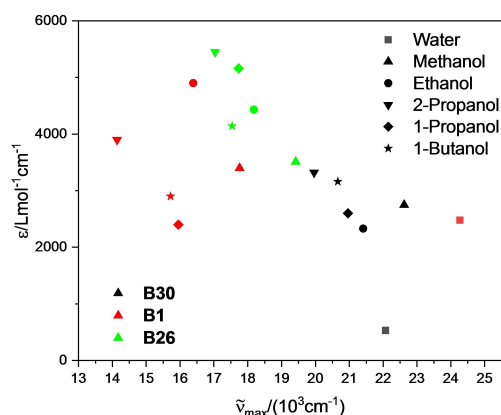


Figure 3. Correlation of the molar absorption coefficient ϵ at the UV/Vis peak maximum $\epsilon(\tilde{\nu}_{max})$ as a function of the absorption energy ($\tilde{\nu}_{max}$ in cm^{-1}) of **B30**, **B1** and **B26** for simple alcohols and H_2O .

B26 and **B30** contain *tert.* butyl or phenyl as sterically demanding groups in the vicinity of the phenolate oxygen. Therefore, the interaction is dominated by the electromagnetically determined term $f(n)$ (=Lorentz-Lorenz relation) or the number of dipoles per unit volume (N), while in **B1** the formation of hydrogen bonds additionally interferes the electrostatic interaction. However, the correlation of absorption energy with $f(n)$ is reasonably recognizable as long as 1,2-ethandiol or aromatic alcohols are not taken into account.

Overall, calculating the linear correlations of $\epsilon(\tilde{\nu}_{max})$ as a function of $\tilde{\nu}_{max}$, individual correlations for HBD and non-HBD solvents can be seen, as described in many publications on **B30**.^[1,2,7]

From eq. (4), the $\epsilon(\tilde{\nu}_{max})$ of **B30** for water is estimated to be $530 \text{ Lmol}^{-1} \text{ cm}^{-1}$. It is not given in Ref. [7] This is why **B30** cannot be readily measured in water; not only because of its poor solubility but also because of the low ϵ . Therefore, the $E_T(30)$ value for water could only be measured with a 10 cm long cuvette using a saturated **B30** solution.^[52] This finding is completely in line with assuming that coupling contributes a major part to **B30**'s $\epsilon(\tilde{\nu}_{max})$ as water has a comparably weak absorption band in the deep UV, located at about 68000 cm^{-1} with an $\epsilon(\tilde{\nu}_{max})$ of only about $1700 \text{ l mol}^{-1} \text{ cm}^{-1}$.^[54] H_2O could also be seen as alcohol without C-H groups for which, due to the absence of C-H groups, the $n \rightarrow \sigma^*$ has the highest oscillator position and the corresponding O-H bands the lowest intensity compared to the alcohols. In this particular case the application of Bayliss' simplified model should be possible, as only very weak coupling would be expected.

Extending the discussion to more HBD solvents and, also, to non-HBD solvents, separate individual correlations can be recognized (eqs. 5a and 5b, cf. Figure S1 and S2).

$$\epsilon(\tilde{\nu}_{max})(\mathbf{B30})(\text{HBD}) = -777 \cdot \tilde{\nu}_{max} 10^{-3} + 18115 \quad (5a)$$

$$R^2 = 0.8086 \quad (R = 0.89), \quad n = 11$$

$$\epsilon(\tilde{\nu}_{max})(\mathbf{B30})(\text{non-HBD}) = -1796 \cdot \tilde{\nu}_{max} 10^{-3} + 33360 \quad (5b)$$

$$R^2 = 0.808 \quad (R = 0.89), \quad n = 25$$

The decrease in $\epsilon(\tilde{\nu}_{max})$ is more pronounced for non-HBD solvents (greater slope $\Delta\epsilon/\Delta\nu$ with -1796) than for HBD solvents (lower slope $\Delta\epsilon/\Delta\nu$ with -777), the difference between the two solvent types is evident.

Overall, above findings are not in line with the currently prevalent explanation of solvatochromism of negative solvatochromic dyes, which is that the interactions of the solute molecule with the molecules of the solvent change the energy of the HOMO and the LUMO, so that the frequency of light absorption is shifted.^[2,3] Additionally, above effect introduced by the polarization of matter through light as modelled by the Lorentz-Lorenz model has to be considered. It is important to realize that it only exists if actually light is shone on the solution, but that the modern explanation requires that the interactions persist also in the dark state. In other words, recording an UV/Vis spectrum changes the state of matter

through polarization and the recorded spectrum does reflect this polarized state. Quantum chemical calculations performed to understand this finding must take into account not only chemical interactions between solute and solvent, but also the polarizing effect of light on matter. Often the solvent is only taken into account as a dielectric continuum while a fully quantum-mechanical treatment would be necessary, which is computationally costly.^[53–56]

The polarity of **B30** is concentration dependent, as ¹³C NMR experiments show.^[20] With increasing the solute (**B30**) concentration, the polarity of the dye decreases according to the modern view. An alternative explanation is that increasing concentration is equivalent with increasing oscillator strengths, which leads to redshifts following eq. (2) in agreement with Bayliss' simplified model.^[43] For the structurally related dyes **B1** and **B26** (Scheme 1), similar plots ϵ as function of $\tilde{\nu}_{\max}$ are found as shown in eq. 6 and 7a, b and c as well as Figure S3 and Figure S4 in the ESI section. It should be noted that dye **B1** was only measured in HBD solvents because of its poor solubility in aprotic solvents.

$$\epsilon(\tilde{\nu}_{\max})(\mathbf{B1})(\text{HBD}) = -181 \cdot \tilde{\nu}_{\max} 10^{-3} + 6711. \quad (6)$$

$$R^2 = 0.6696 \quad (R = 0.814), n = 9$$

The deviating solvents are discussed in the ESI part.

The dye **B26** is more hydrophobic. It is also soluble in weakly polar solvents like benzene, but insoluble in water and polyols.

$$\epsilon(\tilde{\nu}_{\max})(\mathbf{B26})(\text{all solvents}) = -2434 \cdot \tilde{\nu}_{\max} 10^{-3} + 42760. \quad (7a)$$

$$R^2 = 0.8225 \quad (R = 0.91), n = 26$$

$$\epsilon(\tilde{\nu}_{\max})(\mathbf{B26})(\text{non-HBD}) = -3606 \cdot \tilde{\nu}_{\max} 10^{-3} + 57958. \quad (7b)$$

$$R^2 = 0.92 \quad (R = 0.96), n = 16$$

$$\epsilon(\tilde{\nu}_{\max})(\mathbf{B26})(\text{HBD solvents}) = -983 \cdot \tilde{\nu}_{\max} 10^{-3} + 19531. \quad (7c)$$

$$R^2 = 0.4644 \quad (r = 0.68), n = 10$$

The diagrams for equations 5, 6 and 7 are shown in the ESI part.

From the results of the correlation analyses it can be seen that regardless of the substitution pattern of the dye and solvent set used, there is always a more or less linear correlation of $\epsilon(\tilde{\nu}_{\max})$ versus $\tilde{\nu}_{\max}$. With increasing polarity, a blue (hypsochromic) UV/Vis-shift associated with a decrease in $\epsilon(\tilde{\nu}_{\max})$ can be observed.

Notably, there are some particular results which are of importance:

In HBD solvents, the susceptibility (slope) as function of polarity is significantly smaller compared to non-HBD solvents. According to the modern view, the formation of hydrogen bonds at the phenolate-betaine dye alters the inherent dipole moment of the dye, which is reflected in an additional influence

of the global polarity of the solvent on $\epsilon(\tilde{\nu}_{\max})$ and $\tilde{\nu}_{\max}$ as recently discovered.^[26]

Thus, hydrogen bonding in combination with high global polarity has a stronger effect on lowering the inherent dipole moment of the dye. Therefore, changes in the polarity of solvents that cannot form H-bridges have a stronger effect on the changes in $\epsilon(\tilde{\nu}_{\max})$, because H-bridges have a damping, levelling effect. Hence, in HBD solvents, $\epsilon(\tilde{\nu}_{\max})$ is significantly lower compared to non-HBD solvents regardless the substitution pattern of the dye.

Therefore, regardless whether HBD or non-HBD solvents are considered, the decrease of $\epsilon(\tilde{\nu}_{\max})$ with increasing polarity can only be partly attributed to a lowering of the transition dipole moment of **B30** caused by the impact of the polarity of the solvent.

Obviously, the related change of oscillator strength and coupling between the oscillators of solute and solvent as well as complex concentration effects of the solvent volume in relation to the dye play an additional role,^[10,11,25] which is the subject of further investigations. The particularly clear trend correlations of $\tilde{\nu}_{\max}/\epsilon$ as function of N in HBD solvents have led us to re-evaluate the global polarity of HBD solvents in light of the results of this work, which will be presented in a following paper.^[57] Especially, the special role of polyhydric alcohols will be studied more profoundly.

Conclusion

Relationships of UV/Vis peak positions and the corresponding molar absorption coefficient $\epsilon(\tilde{\nu}_{\max})$ of negative solvatochromic dyes of the Reichardt type are examined. This relationship is explained via electromagnetic coupling of electronic excitations of the solute and the solvent as a consequence of the polarization of matter by light. According to the Lorentz-Lorenz relation, which allows to model the effect under simplifying assumptions, an increase of oscillator strength or a redshift of oscillator positions of the solvent cause a corresponding redshift and molar extinction coefficient increase of the solute. This effect is supposed to exist also in case of positive solvatochromic dyes, for which it must be overcompensated by other effects. We think that based on these findings a careful reinvestigation of the field of solvatochromism is necessary under consideration of all possible effects that can contribute to find a unified approach which can cover all important aspects of solvatochromism.

Acknowledgements

This study was kindly supported by the Leibniz Institute of Photonic Technology, Jena, Germany, and the University of Technology Chemnitz, Institute of Chemistry, Chemnitz, Germany. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: solvatochromism · Kundt's rule · Lorentz-Lorenz relation · Reichardt's dye · UV/Vis spectroscopy

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Manuscript received: February 10, 2022
Revised manuscript received: May 17, 2022
Accepted manuscript online: May 17, 2022
Version of record online: June 17, 2022