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Solvent and temperature effects on the electronic transitions of 3-*H*-indolo-2-dimethinehemicyanine dyes

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Abstract

Solvent effects on the UV/vis absorption spectra of five hemicyanine dyes **1**, obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** with different substituted anilines **3**, have been investigated. Analysis of the observed hypsochromic shifts using Reichardt's single parameter solvent polarity scale (E_T^N) revealed that the dye obtained with 4-aminophenol is the most sensitive to solvent effects. Multiple regression analysis based on the Kamlet–Taft equation indicated that (i) the hydrogen bond donor properties and the dipolarity/polarizability of the solvent have an equal contribution to the solvatochromic behavior of the dye obtained with aniline, and (ii) the hydrogen bond accepting properties of the solvent have a significant contribution to the solvatochromic behavior of the 3-hydroxy-substituted dye. UV/vis absorption spectra were also recorded in mixtures of water and 2-propanol. A preferential solvation in 2-propanol was observed and quantified for all dyes. Finally, the effects of the temperature on the solvatochromism in binary mixtures were also investigated in order to reveal the susceptibilities of dye–water–propanol interactions. Increasing temperatures produced a depletion of the 2-propanol in the solvation shell of the hemicyanines.

Keywords: Hemicyanine dyes; Solvatochromism; Thermosolvatochromism; Solvent polarity scale; Kamlet–Taft equation; Binary solvent mixtures

1. Introduction

Taking into account that the solvent can significantly influence the chemical and physical properties of the solute, the investigation of solvent–solute interactions is very important. In the case of hemicyanine dyes such investigations bear great practical importance due to the extensive use of such dyes in the textile industry [1].

Solvatochromism is caused by the different solvation of the ground and first excited states of the light-absorbing molecule and thus it is a convenient tool to study the nature of solvent–solute interactions. Using solvatochromism the existence of specific (acid–base) and/or non-specific (dipolar/polarizable) solvent–solute interactions can be revealed and quantified. The solvatochromism of different probes has already been used to study retention processes in reversed-phase liquid chromatography [2,3], to probe the surface polarity of different materials (such as gold-cluster-functionalized silica particles [4] or solid acid catalysts [5]), to investigate the solvent properties of ionic liquids [6,7] and solvent mixtures [8], and to detect water in aprotic solvents at concentrations below 50 ppm [9].

Two of the most used quantitative treatments of the solvent effects are the $E_T(30)$ (or E_T^N in its normalized version) scale introduced by Reichardt (see [10] and references therein) and the multiparametric equation introduced by Kamlet and

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Taft, [11–14]. Reichardt's E_T^N scale was derived from the long-wavelength vis/near-IR absorption band of a negatively solvatochromic pyridinium *N*-phenolate betaine dye. Such solvent polarity scales, based on spectral data of a single indicator dye, can be applied only if the solute–solvent interactions of the examined dye are similar to those of the reference indicator dye [15]. The Kamlet–Taft multiparameter equation (a linear solvation energy relationship) associates each kind of solute–solvent interaction with a separate parameter:

$$\nu_{\max}(\text{solute}) = \nu_{\max,0} + a\alpha + b\beta + s(\pi^* + \mathrm{d}\delta)$$

where $\nu_{\max}$(solute) is the position of the UV/vis absorption band in the given solvent, $\nu_{\max,0}$ is the position of the UV/vis absorption band in a reference system (such as a non-polar medium, e.g. cyclohexane), α characterizes the hydrogen bond donating (HBD) ability of the solvent, β characterizes the hydrogen bond accepting (HBA) ability of the solvent, and π^* the dipolarity/polarizability of the solvent. δ is the polarizability correction term, which is 1 for aromatic solvents, 0.5 for polyhalogenated solvents, and 0 for aliphatic solvents. The factors a, b, and s are solvent-independent correlation coefficients (i.e. constants characteristic for the solute). Their magnitudes and signs indicate the relative contribution of the respective solvent–solute interaction to the electronic transition energy.

While investigations in pure solvents can reveal details of the solvent–solute interactions, the study of solvatochromism in binary mixtures can also reveal details of the solvent–solvent interactions and thus on the relationship between the composition of the probe solvation microsphere and that of the bulk solvent [16,17]. Moreover, the study of the effects of temperature on the solvatochromism in binary mixtures (i.e. thermosolvatochromism) can provide information on the susceptibilities of these solvent–solvent interactions to changes in temperature [16,17].

It is the purpose of this study to investigate the solvatochromic behavior of five hemicyanine dyes **1** obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** with different substituted anilines **3**. Solvent effects on the longest wavelength UV/vis absorption band of the hemicyanine dyes will be quantified using both Reichardt's E_T^N solvent polarity scale and the Kamlet–Taft multiparameter equation. Moreover, the thermosolvatochromism of these dyes in binary mixtures of water and 2-propanol will be investigated in order to obtain a thorough picture on the possible solvent–solute and solvent–solvent interactions.

2. Materials and methods

2.1. Materials

Aniline, 4-aminophenol, 3-aminophenol, 4-ethylaniline, 3-ethylaniline, and glacial acetic acid were purchased from Merck. Spectroscopic quality acetonitrile, chloroform, dichloromethane, ethyl acetate, methanol, 2-propanol, dimethylsulfoxide, and tetrahydrofuran were also purchased from Merck. (1,3,3-Trimethylindolin-2-ylidene)acetaldehyde was synthesized as previously described [18,19]. NaCl and $KClO_4$ were purchased from Chimopar. Aqueous solutions were prepared using demineralized and twice-distilled water.

2.2. Synthesis and characterization of hemicyanine dyes

Hemicyanine dyes **1** were obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** with aniline, 4-aminophenol, 3-aminophenol, 4-ethylaniline, or 3-ethylaniline according to a procedure described previously [20]. A mixture of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** (0.01 mol), the corresponding aniline **3** (0.01 mol), and glacial acetic acid (5 ml) was stirred at room temperature for 15–30 h. Then the mixture was diluted with water (25 ml), and salted out with either NaCl or $KClO_4$. $KClO_4$ was only used to salt out the condensation products, which did not precipitate with NaCl. The precipitate was filtered, washed first with water, and then with ethanol and ether. The dye was finally recrystallized from methanol.

The structure and purity of dyes **1** was confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were recorded on a Gemini 300 (300 MHz) spectrometer, using hexadeuterated dimethylsulfoxide (DMSO-d_6) as solvent, at room temperature. Chemical shifts are expressed in δ ppm using tetramethylsilane (TMS) as internal standard. The dyes **1** were characterized also by melting points and IR spectra. The melting points were recorded with a Böetius type apparatus (equipped with a HMK05 observation system) and are presented uncorrected. The IR spectra were recorded as KBr pellets with a Nicolet Impact 410 FT-IR spectrometer.

2.3. Spectrophotometric investigation of the solvatochromism

The UV/vis spectra of the investigated compounds were recorded on a Cintra 10e GBC spectrophotometer, at 25 °C excepting the thermosolvatochromic behavior, which was studied on a Specord 205 spectrophotometer (Analytik Jena AG, Germany) between 25 °C and 45 °C. An Ecoline 200 thermostat (Lauda GmbH, Germany) was used to maintain temperatures (±0.01 °C). Spectroscopic quality solvents were used throughout the study to prepare the dye solutions (having concentrations between 2.90 and 2.92×10^{-5} mol l^{-1}). The absorption spectra of freshly prepared dye solutions were recorded between 200 nm and 600 nm. All dyes displayed an intense and sharp absorption band around 400 nm. The exact position of this band was influenced by the nature of the solvent and temperature. The E_T^N solvent polarity parameters given by Reichardt's review [10] were used. For the Kamlet–Taft solvent parameters (i.e. α, β, and π^*) several publications were reviewed, and the most often used values were considered [4,21–24].

3. Results and discussion

The structure and purity of the synthesized dyes was confirmed by ^{1}H NMR spectroscopy (Table 1) and IR

Table 1
^{1}H NMR data (chemical shift δ [ppm], number of protons, and coupling constant J [Hz]) for the compounds **1a–1e**

Dye (Scheme 1)	Type of protons and multiplicity					
	$>C(CH_3)_2$, s	$\overset{\delta^+}{-NCH_3}$, s	H_a, d	H_b, d	H_{ar}, m	$\overset{\delta^+}{--NH-}$, s/d	Substituent protons
1a	1.67; 6H	3.63; 3H	6.34; 1H; $J = 12.5$	8.63; 1H; $J = 12.5$	7.2–7.7; 9H	12.38; 1H; d; $J = 12.5$	–
1b	1.65; 6H	3.59; 3H	6.29; 1H; $J = 12$	8.5; 1H; $J = 12$	7.2–7.6; 8H	Not recorded	$\delta_{OH} = 9.98$; s; 1H
1c	1.66; 6H	3.63; 3H	6.25; 1H; $J = 12.4$	8.57; 1H; $J = 12.4$	6.6–7.7; 8H	12.66; s; 1H	$\delta_{OH} = 10.02$; s; 1H;
1d	1.69; 6H	3.66; 3H	6.08; 1H; $J = 12.2$	8.63; 1H; $J = 12.2$	7.2–7.8; 8H	11.92; s; 1H	$\delta_{CH_2-CH_3} = 1.20$ t; 3H; $J = 7.0$; $\delta_{CH_2-CH_3} = 2.64$, q; 2H; $J = 7.0$;
1e	1.7; 6H	3.67; 3H	6.13; 1H; $J = 12.4$	8.64; 1H; $J = 12.4$	7.1–7.7; 8H	11.96; s; 1H;	$\delta_{CH_2-CH_3} = 1.23$ t; 3H; $J = 7.6$; $\delta_{CH_2-CH_3} = 2.69$, q; 2H; $J = 7.6$

s = singlet; d = doublet; t = triplet; q = quartet; m = complex multiplet.

spectroscopy (Table 2). Some additional properties of the obtained hemicyanines are also listed in Table 2.

Organic dyes with a polarizable conjugated π-electron system exhibit absorption bands in the visible region due to a charge transfer between an electron donor moiety (the auxochrome) and an electron acceptor moiety (the chromophore). As shown in Scheme 1, the hemicyanines discussed in the present work have an ionic conjugation in which the electron acceptor moiety is cationic. Such dyes are ionic in both their ground and excited states, and thus the electronic transition causes only small polarity changes. These small polarity changes are expected to cause only small solvatochromic shifts with the increasing solvent polarity [15].

Fig. 1 shows a typical example of the observed solvent effect. For an easier comparison, each spectrum was also normalized to its maximum absorbance and the obtained relative absorbances are depicted in the inset of Fig. 1.

The position of the UV/vis absorption maxima of all dyes ($\nu_{\mathrm{experimental}}$), along with the Kamlet–Taft and Reichardt's solvent parameters are presented in Table 3. Although the use of a wide spectrum of solvents was attempted (polar and non-polar, protic and aprotic, HBD and HBA), the poor solubility of the dyes in non-polar solvents caused some limitations. As shown in Table 3, all the investigated dyes display a small hypsochromic shift with the increasing solvent polarity, that is, they are characterized by a negative solvatochromism.

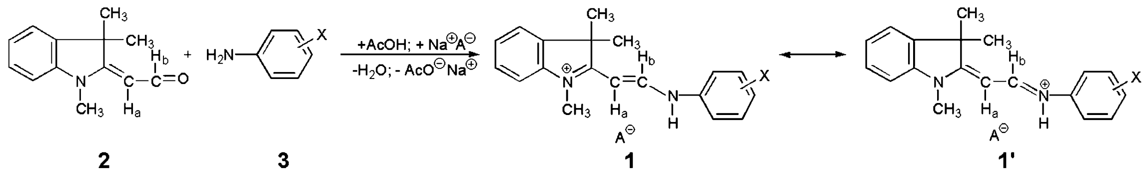
The observed hypsochromic shift was analyzed using both Reichardt's E_T^N solvent polarity scale, and the Kamlet–Taft multiparameter equation.

Fig. 2 shows a typical plot of the position of absorption maximum (ν_{measured}, cm^{-1}) as a function of Reichardt's E_T^N solvent parameter. The equations describing the correlation between ν_{measured} and E_T^N for all the studied hemicyanines are listed in Table 4. Good correlation coefficients ($R = 0.9243–0.9887$) were observed only after excluding data points obtained in acetonitrile (i.e. data found in acetonitrile do not fit the model). The slopes of the plots indicate that the dyes obtained with aminophenols ($\Delta\nu_{\mathrm{measured}}/\Delta E_T^N = 1301$ and 1178 cm^{-1} for 4-aminophenol and 3-aminophenol, respectively) are more sensitive to solvent effects than the dyes obtained with aniline, 4-ethylaniline, and 3-ethylaniline ($\Delta\nu_{\mathrm{measured}}/\Delta E_T^N = 975$, 860 and 775 cm^{-1}, respectively). This is in line with an increased ability of the OH group to interact with HBD and HBA solvents. The good correlations obtained with the E_T^N scale (even though after omitting acetonitrile) are somewhat surprising taking into account that poor correlations were previously reported for probes able to form solute-to-solvent hydrogen bonds through the amine hydrogen atoms [23].

When analyzing the solvatochromic data by the Kamlet–Taft multiparameter equation, the F-ratio (related to the analysis of variance, ANOVA) was used to determine (i) the solvatochromism of which dye is described by the multiparameter equation, and (ii) which terms of the equation are statistically significant in fitting. This approach was recently described in the literature [23]. If F increases, when a new variable (i.e. π^*, α, or β) is introduced, the term is retained; conversely, if F decreases the term is rejected [23]. The statistical analyses were performed with Origin 7.5 software (from OriginLab Corporation, USA), after excluding the data obtained in acetonitrile (for all dyes but the hemicyanine based on 3-aminophenol), and polychlorinated solvents (for all dyes because their introduction implies the use of an additional

Table 2
Some chemical and physical–chemical properties of the synthesized compounds

Dye (Scheme 1)	X	Melting point (°C)	Yield of synthesis (%)	$\nu_{\max}$ (cm^{-1})	
				ν_{NH}	δ $\mathrm{H{>}C{=}C{<}H}$
1a	H	129–131	89.00	3385	928
1b	4-OH	254.5–257.5	69.25	3390	931
1c	3-OH	243–245	82.00	3323	929
1d	4-C_2H_5	211–213	89.02	3291	924
1e	3-C_2H_5	186.5–188.5	76.20	3294	932



Scheme 1. Synthesis and resonance forms of the investigated hemicyanine dyes (X = H, $A^- = Cl^-$; 4-OH, $A^- = Cl^-$; 3-OH, $A^- = Cl^-$; 4-C_2H_5, $A^- = ClO_4^-$; 3-C_2H_5, $A^- = ClO_4^-$).

correction parameter, δ). UV/vis absorption data obtained for several azo dyes in acetonitrile and chloroform [22], and for 1,3-bis-substituted-5,5-dimethylhydantoins in acetonitrile and diethyl ether [25] have previously been observed not to fit multiple regressions to Kamlet–Taft solvent parameters.

Surprisingly, for the hemicyanines obtained with 4-aminophenol, 4-ethylaniline, and 3-ethylaniline the F-statistic was very low (<50) for all multiple regressions based on any equation of two or three terms. Larger values of F-statistic (>100) were obtained for the hemicyanine based on 3-aminophenol (using an equation containing all three terms) and for the hemicyanine based on aniline (using an equation containing π^*, and α terms). The corresponding theoretical Kamlet–Taft equations are listed in Table 4. According to these multiparameter equations (i) the hemicyanine dye obtained with aniline is equally sensitive to the dipolarity/polarizability and the HBD properties of the solvent and it is not influenced by the HBA ability of the solvent; (ii) the hemicyanine dye bearing a *meta* hydroxyl group is more sensitive to the HBA and HBD abilities of the solvents than to the dipolarity/polarizability of the solvents. These results are chemically reasonable taking into account that the insertion of a hydroxyl group in the structure of the dye enhances the hydrogen bond donor ability of the respective dye (i.e. such dye will interact stronger with HBA solvents) and that our dyes are positively charged both in ground and excited states and therefore not much affected by solvent dipolarity/polarizability. However, the HBD and HBA abilities of the solvents have opposite effects on the position of maximum absorption of the 3-OH-substituted dye (the negative sign of b coefficient indicating a bathochromic shift which is never observed experimentally). The excellent fit of the experimental data (ν_{measured}) and the absorption maxima calculated with the theoretical equations ($\nu_{\text{calculated}}$) (see Fig. 3) prove that the Kamlet–Taft model predicts well the position of maximum absorption in solvents of different polarity, and different HBD and HBA properties (at least for the hemicyanines obtained with aniline and 3-aminophenol).

The above results also prove the usefulness of solvatochromic data obtained in pure solvents to reveal the nature and extent of solvent–solute interactions. However, very often, the use of solvent mixtures is necessary (for example in chromatographic separations). In the case of solvent mixtures the situation is further complicated by solvent–solvent interactions. A combination of solvent–solute and solvent–solvent interactions will change the composition of the solvation microsphere relative to that of the bulk solvent, and deviations from the ideal behavior of the solvatochromic probes occur. Preferential solvation appears due to non-specific dielectric enrichment (i.e. enrichment of the solvation shell due to probe-dipole–solvent-dipole interactions) and specific probe–solvent interactions (such as hydrogen bonding). Together with solvent microheterogeneity (i.e. one component of the

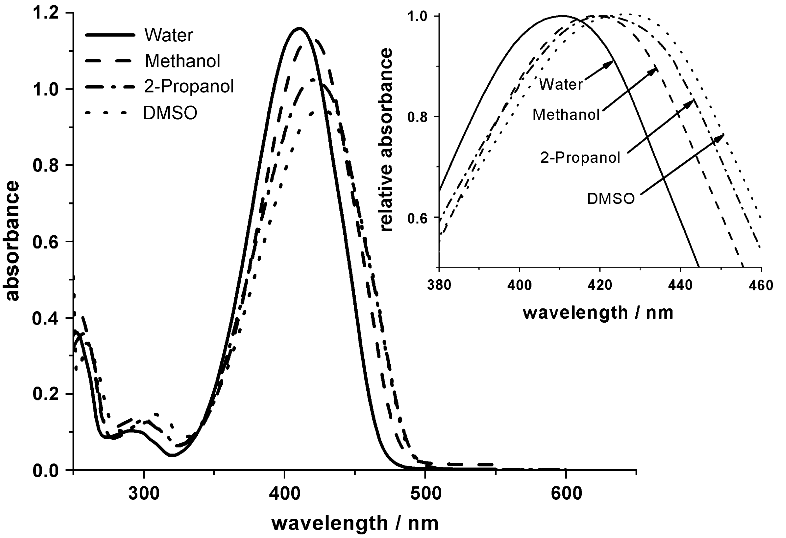


Fig. 1. Visible absorption spectra of the hemicyanine dye obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde with 4-aminophenol in different organic solvents.

Table 3
The position of the longest wavelength absorption maxima of five hemicyanine dyes measured in different solvents and the empirical Kamlet–Taft and E_T^N solvent parameters

Solvent	$\nu_{\text{experimental}}$ (cm^{-1}) for hemicyanines obtained with					E_T^N	Kamlet–Taft solvent parameters			
	Aniline	4-Aminophenol	3-Aminophenol	4-Ethylaniline	3-Ethylaniline		π^*	α	β	δ
Tetrahydrofuran	23 923	–[a]	–[a]	23 725	23 895	0.207	0.58	0	0.55	0
Ethyl acetate	23 923	–[a]	–[a]	23 866	24 010	0.228	0.55	0	0.45	0
Chloroform	23 810	23 419	23 585	23 557	23 810	0.259	0.58	0.2	0.1	0.5
Dichloromethane	23 895	–[a]	–[a]	23 669	23 923	0.309	0.82	0.13	0.1	0.5
Dimethylsulfoxide	24 155	23 529	23 923	23 810	23 895	0.444	1	0	0.76	0
Acetonitrile	24 390	24 038	24 272	24 213	24 390	0.46	0.75	0.19	0.31	0
2-Propanol	24 213	23 781	24 010	23 981	24 155	0.546	0.48	0.76	0.95	0
Methanol	24 390	23 923	24 272	24 155	24 272	0.762	0.6	0.93	0.62	0
Water	24 631	24 390	24 480	24 361	24 510	1	1.09	1.17	0.47	0

[a] Not soluble.

binary mixture prefers a molecule of the same type) preferential solvation is the main source of non-ideal behavior of solvatochromic probes in binary solvent mixtures [16,17].

The solvatochromic behavior of three hemicyanine dyes was investigated in water–2-propanol mixtures in order to reveal the extent of preferential solvation and solvent microheterogeneity. The effect of the temperature on the observed solvatochromism was subsequently also studied in order to reveal the susceptibilities of dye–water–propanol interactions to changes in temperature. As shown in Fig. 4, the position of the absorption maximum of the 3-aminophenol-based dye shifts to smaller wavelengths with increasing mole fractions of water in water–2-propanol mixtures (as expected from the above findings).

The ideal behavior of the dye in such experiments is given by the following equation [26]:

$$\nu_{\text{ideal}} = x_1\nu_1 + (1 - x_1)\nu_2$$

where ν_1, and ν_2 are the dye's spectral responses in the pure solvents, and x_1 is a mole fraction. This equation indicates that the expected spectral response of the hemicyanine dye in a binary solvent mixture is a mole fraction weighted average of the spectral responses in the two pure solvents. Fig. 5 shows the experimentally observed variation of the position of maximum absorption with the mole fraction of water compared to the ideal behavior described by the above equation. A pronounced deviation from the theoretical linearity can be observed at water mole fractions ranging between 0.51 and 0.97 for all the studied dyes. The deviation indicates a higher fraction of 2-propanol in the solvation shell than in the bulk solvent in the respective range of mole fractions. Such a behavior can be explained by preferential solvation and solvent microheterogeneity.

In the case of 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, 1-methylquinolinium-8-olate and 4-[2-(1-methylpyridinium-4-yl)ethenyl]phenolate a similar behavior was explained by the preferential solvation in alcohols due to hydrophobic dye–alcohol interactions and H-bonding [27]. The authors also reveal that solvation by alcohols was affected more by hydrophobic probe–alcohol interactions than by hydrogen bonding [27]. This could be the case of our hemicyanines as well taking into account that the insertion of a hydroxyl group (i.e. of a hydrogen bond donor) in the dye structure did not change significantly the behavior of the dye in the binary solvent mixtures (see data for aniline- and aminophenol-based dyes in Fig. 5).

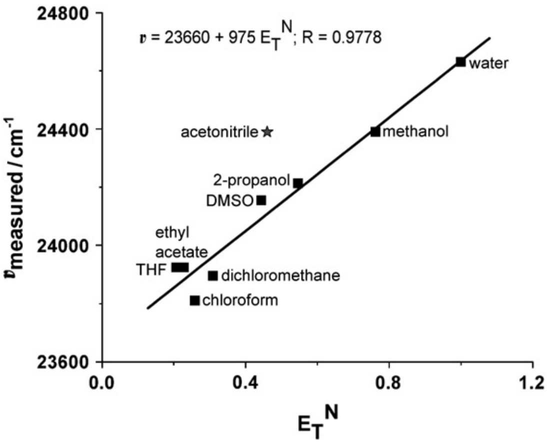


Fig. 2. Position of the longest wavelength absorption maximum of the hemicyanine obtained with aniline as a function of the Reichardt E_T^N solvent polarity parameter.

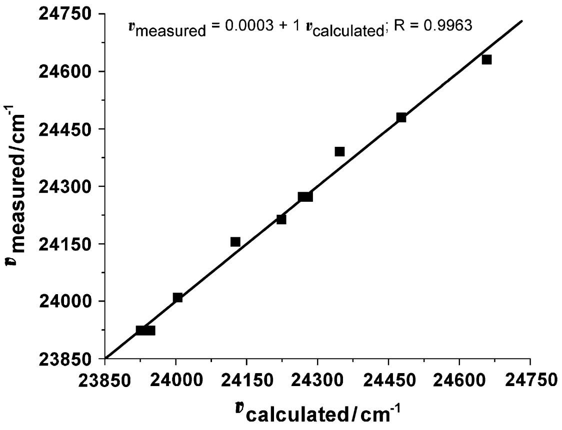


Fig. 3. ν_{measured} vs. $\nu_{\text{calculated}}$ plots for hemicyanines obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde with aniline and 3-aminophenol. The calculated values were obtained using the theoretical Kamlet–Taft equations displayed in Table 4.

Table 4
Solvatochromic behavior of the investigated hemicyanines as described using Reichardt's solvent polarity scale and the Kamlet–Taft solvatochromic parameters

Hemicyanine obtained with	Reichardt's solvent polarity scale	Kamlet–Taft multiparameter equation
Aniline	$\nu = (23\,660 \pm 46) + (975 \pm 85)E_T^N$, $R = 0.9778$	$(23\,698 \pm 49) + (428 \pm 66)\pi^* + (421 \pm 32)\alpha$, $R^2 = 0.9889$; $F = 134$
4-Aminophenol	$\nu = (23\,025 \pm 101) + (1301 \pm 154)E_T^N$, $R = 0.9796$	–
3-Aminophenol	$\nu = (23\,345 \pm 67) + (1178 \pm 103)E_T^N$, $R = 0.9887$	$(24\,378 \pm 30) + (51 \pm 24)\pi^* + (303 \pm 11)\alpha - (661 \pm 24)\beta$, $R^2 = 0.9994$; $F = 545$
4-Ethylaniline	$\nu = (23\,487 \pm 78) + (860 \pm 145)E_T^N$, $R = 0.9243$	–
3-Ethylaniline	$\nu = (23\,695 \pm 67) + (775 \pm 123)E_T^N$, $R = 0.9317$	–

The microheterogeneity of the water–2-propanol mixtures can be another cause of the observed non-ideal behavior. Indeed, a Rayleigh light scattering study found that (i) at mole fractions of water $x_w > 0.95$, 2-propanol is well solvated by water molecules, and hydrates consisting of one 2-propanol molecule and 20–30 water molecules are formed in the mixtures, and (ii) at mole fractions of water $0.7 < x_w < 0.95$ large clusters mainly composed of 2-propanol molecules are formed in the mixtures, and these clusters are further reduced into small 2-propanol aggregates at $x_w < 0.6$ [28]. The solvatochromic behavior of our hemicyanines appear to sense the transition from 2-propanol clusters to well solvated 2-propanol molecules at $x_w > 0.6$ (one can expect that the increased solvation of 2-propanol depletes of water the solvation shell of the hemicyanines).

As a final step of our investigations on the solvent–solute and solvent–solvent interactions in solutions of hemicyanine dyes, we have studied the susceptibility of these interactions to changes in temperature. The position of maximum absorption was determined for the 3-aminophenol-based hemicyanine in different water–2-propanol mixtures at five temperatures between 25 °C and 45 °C. Significant deviations from the ideal behavior were observed at all temperatures (due to preferential solvation and microheterogeneity of the binary mixture). The extent of the observed deviation was temperature dependent. The extent of the deviation from ideality, δ_{s2}, was calculated using the following equations according to a previously published work [29]:

$$x_2^L = (E_{12} - E_1)/(E_2 - E_1)$$

$$\delta_{s2} = x_2^L - x_2$$

where E_{12} is defined as the excitation energy (kcal mol^{-1}) of any indicator and can be calculated from the wavelength of the maximum of the long-wavelength absorption band, $E_{12} = 28\,591/\lambda$ (nm), E_1 and E_2 are the values of the electronic transition energy in the solvents 1 and 2, respectively, x_2 is the mole fraction of the solvent 2 in the bulk, while x_2^L is that in the solvation microsphere. Fig. 6 shows the deviation from the ideal behavior, δ_{s2}, as a function of water mole fraction, at different temperatures. The solvatochromic behavior of the hemicyanine dyes was significantly influenced by temperature only in binary mixtures containing water in mole fractions $0.32 < x_w < 0.86$. Increasing temperatures caused an increase of the water content of the solvation shell in the

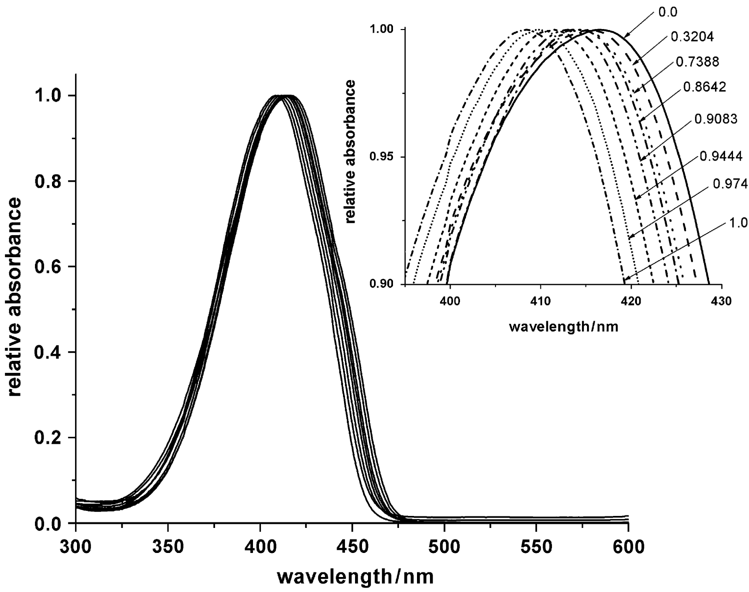


Fig. 4. Visible absorption spectra of the hemicyanine dye obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde with 3-aminophenol in water–2-propanol mixtures containing different mole fractions of water.

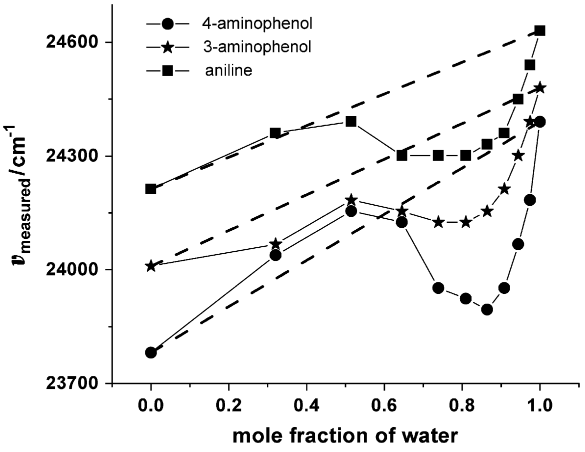


Fig. 5. Dependence of the position of maximum absorption on the mole fraction of water in binary mixtures of water–2-propanol for hemicyanines obtained with the indicated anilines. The diagonal lines represent the expected behavior if solvatochromism was ideal.

mentioned region of water mole fractions. Therefore, the temperature affects 2-propanol more than it affects water, and this leads to a measurable depletion of alcohol in the probe solvation shell as also observed by others [30].

4. Conclusions

The solvent effects on the UV/vis absorption spectra of five hemicyanine dyes (obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde with aniline, 4-aminophenol, 3-aminophenol, 3-ethylaniline, or 4-ethylaniline) were investigated. When increasing the polarity of the solvent, all dyes displayed a small (~15 nm) hypsochromic shift of their longest wavelength absorption maximum. This solvatochromism was then analyzed using Reichardt's single parameter E_T^N polarity scale and the multiparameter Kamlet–Taft equation. Correlations with Reichardt's single parameter E_T^N polarity scale indicated the dye obtained with 4-aminophenol as the most sensitive to solvent effects ($\Delta\nu/\Delta E_T^N = 1301\ \text{cm}^{-1}$). Multiple regression analysis based on the Kamlet–Taft equation indicated that the hemicyanine dye obtained with aniline is sensitive to the dipolarity/polarizability and the HBD properties of the solvent but not to HBA ability of the solvent, while the hemicyanine dye bearing a *meta* hydroxyl group is more sensitive to the HBA and HBD abilities of the solvents than to the dipolarity/polarizability of the solvents. The solvatochromism of the hemicyanine dyes was also investigated in mixtures of water and 2-propanol. Due to preferential solvation and solvent microheterogeneity, the solvation shell of the dyes was enriched in 2-propanol compared to the bulk composition. Dyes with and without hydroxyl group in their structure displayed a rather similar preferential solvation suggesting that hydrophobic interactions are more important than hydrogen bonding in this phenomenon. At water mole fractions of $0.32 < x_w < 0.86$, the hemicyanine–2-propanol interaction was found to be more susceptible to temperature effects than the hemicyanine–water interaction. Increasing temperatures (25–45 °C) caused a depletion of 2-propanol in the solvation shell and thus a solvatochromic behavior closer to the ideal.

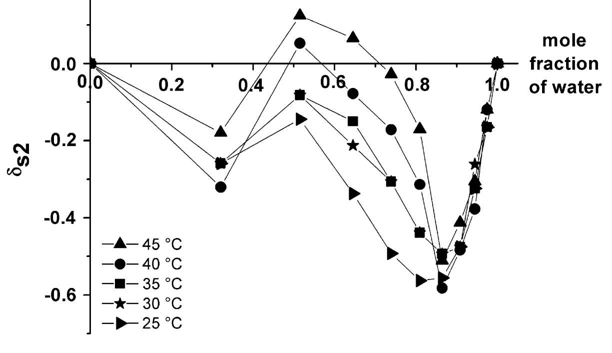


Fig. 6. The extent of the observed deviation from ideal behavior, δ_{s2}, as a function of the mole fraction of water and temperature for the solvatochromic behavior of the 3-aminophenol-based hemicyanine.

References

[1] Raue R. In: Elvers B, Hawkins S, Schulz G, Elvers B, Hawkins S, Schulz G, editors. Ullmann's encyclopedia of industrial chemistry, vol. A16. Wiley-VCH Verlag GmbH and Co. KGaA; 1990. p. 487–534.

[2] Carr PW. Solvatochromism, linear solvation energy relationships, and chromatography. Microchem J 1993;48:4–28.

[3] Sadek PC, Carr PW, Doherty RM, Kamlet MJ, Taft RW, Abraham MH. Study of retention processes in reversed-phase high-performance liquid chromatography by the use of the solvatochromic comparison method. Anal Chem 1985;57(14):2971–8.

[4] Spange S, Kunzmann D, Sens R, Roth I, Seifert A, Thiel WR. Solvatochromic azamethine dyes for probing the polarity of gold-cluster-functionalized silica particles. Chem Eur J 2003;9:4161–7.

[5] Spange S, Sens R, Zimmermann Y, Seifert A, Roth I, Anders S, et al. A solvatochromic dye for probing significantly the dipolarity/polarizability of HBD (hydrogen bond donating) environments. New J Chem 2003;27:520–4.

[6] Reichardt C. Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium *N*-phenolate betaine dyes. Green Chem 2005;7:339–51.

[7] Chiappe C, Pieraccini D. Determination of ionic liquids solvent properties using an unusual probe: the electron donor–acceptor complex between 4,4′-bis(dimethylamino)-benzophenone and tetracyanoethene. J Phys Chem 2006;110:4937–41.

[8] Reichardt C. Pyridinium *N*-phenolate betaine dyes as empirical indicators of solvent polarity: some new findings. Pure Appl Chem 2004;76(10):1903–19.

[9] Pinhero C, Lima JC, Parola AJ. Using hydrogen bonding-specific interactions to detect water in aprotic solvents at concentrations below 50 ppm. Sens Actuators B Chem 2006;114:978–83.

[10] Reichardt C. Solvatochromic dyes as solvent polarity indicators. Chem Rev 1994;94(8):2319–58.

[11] Kamlet MJ, Abboud JM, Taft RW. The solvatochromic comparison method. 6. The π* scale of solvent polarities. J Am Chem Soc 1977;99(18):6027–38.

[12] Kamlet MJ, Abboud JM, Taft RW. An examination of linear solvation energy relationships. Prog Phys Org Chem 1981;13:485–630.

[13] Kamlet MJ, Abboud JLM, Abraham MH, Taft RW. Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters, π*, α, and β, and some methods for simplifying the generalized solvatochromic equation. J Org Chem 1983;48(17):2877–87.

[14] Taft RW, Abboud JLM, Kamlet MJ, Abraham MH. Linear solvation energy relations. J Solution Chem 1985;14(3):153–86.

[15] Arai S, Hida M, Yamagishi T. Solvatochromism of stilbazolium merocyanine-type dyes containing a benzoquinolizinium ring. Dyes Pigments 1995;29(4):263–73.

[16] Tada EB, Silva PL, Tavares C, El Seoud OA. Thermo-solvatochromism of zwitterionic probes in aqueous aliphatic alcohols and in aqueous 2-alkoxyethanols: relevance to the enthalpies of activation of chemical reactions. J Phys Org Chem 2005;18:398–407.

[17] Martins CT, Lima MS, El Seoud OA. . A novel, convenient, quinoline-based merocyanine dye: probing solvation in pure and mixed solvents and in the interfacial region of an anionic micelle. J Phys Org Chem 2005;18:1072–85.

[18] Fritz H. α, β-unsaturated β-anilinocarbonyl compounds as model substances for the chromophore of C-curarine-III (C-fluorocurarine). Chem Ber 1959;92:1809–17.

[19] Panea I, Cristea I. ^{1}H NMR study of condensation products of 1-(2-pyrimidinyl)-3-methylpyrazolin-5-ones with heterocyclic aldehydes. Studia Univ Babes-Bolyai Chem 1996;41(1):9–12.

[20] Gáspár C-L, Panea I, Baldea I. Synthesis and characterisation of 3-*H*-indolo-2-dimethinehemicyanine dyes obtained by the condensation of (1, 3,3-trimethylindolin-2-ylidene)acetaldehyde with anilines in acetic acid. Dyes Pigments 2007;74(2):306–12.

[21] Lagalante AF, Jacobson RJ, Bruno TJ. UV/vis spectroscopic evaluation of 4-nitropyridine *N*-oxide as a solvatochromic indicator for the hydrogen-bond donor ability of solvents. J Org Chem 1996;61:6404–6.

[22] Mijin DZ, Uscumlic GS, Perisic-Janjic NU, Valentic NV. Substituent and solvent effects on the UV/vis absorption spectra of 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones. Chem Phys Lett 2006;418: 223–9.

[23] Moog RS, Kim DD, Oberle JJ, Ostrowski SG. Solvent effects on the electronic transitions of highly dipolar dyes: a comparison of three approaches. J Phys Chem 2004;108:9294–301.

[24] Jacques P. On the relative contributions of nonspecific and specific interactions to the unusual solvatochromism of a typical merocyanine dye. J Phys Chem 1986;90:5535–9.

[25] Uscumlic GS, Kshad AA, Mijin DZ. Synthesis and investigation of solvent effects on the ultraviolet absorption spectra of 1,3-bis-substituted-5,5-dimethylhydantoins. J Serb Chem Soc 2003;68(10):699–706.

[26] Fletcher KA, Baker SN, Baker GA, Pandey S. Probing solute and solvent interactions within binary ionic liquid mixtures. New J Chem 2003;27:1706–12.

[27] Tada EB, Silva PL, El Seoud OA. Thermo-solvatochromism of zwitterionic probes in aqueous alcohols: effects of the properties of the probe and the alcohol. Phys Chem Chem Phys 2003;5:5378–85.

[28] Wu YG, Tabata M, Takamuku T. A Rayleigh light scattering study on mixing states of 2-propanol–water binary mixtures widely used as mobile phase in separation. Talanta 2001;54:69–77.

[29] Fayed T, Etaiw SEH. Preferential solvation of solvatochromic benzothiazolinic merocyanines in mixed binary solvents. Spectrochimica Acta Part A 1998;54:1909–18.

[30] Tada EB, Silva PL, El Seoud OA. Thermo-solvatochromism of betaine dyes in aqueous alcohols: explicit consideration of the water–alcohol complex. J Phys Org Chem 2003;16:691–9.