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Solvatochromism of Nile red in anisotropic media

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ABSTRACT

A quantitative study of the isotropic and anisotropic environment effects on the photophysical properties of a solvatochromic dye, Nile red, was carried out at room temperature. The absorption and emission spectra of the dye in liquid and liquid crystalline media were investigated. The solvatochromic method was used for determining the ground- and excited-state dipole moments. In addition, applicability of solvatochromic method for the dye solvation in anisotropic media was investigated. The nature and degree of the dye–solvent interactions were characterized using multi-parameter solvent polarity analyses.

1. Introduction

Oxazine dyes such as Nile red, NR, are an important group of organic compounds frequently used as an active medium in tuning lasers. The spectral and lasing properties of oxazine dyes are known to be sensitive to their solvent environment [1–3]. NR is a neutral and solvatochromic dye with interesting photophysical properties. It has been shown to be an excellent fluorescence probe for biological systems [4]. This dye exhibits large positive solvatochromism going from non-polar to polar solvents. The strong solvatochromic behavior for NR arises from the fact that it undergoes large dipole moment change during $S_0 \rightarrow S_1$ transition [5,6]. This corresponds to intramolecular charge transfer between diethylamino group and the aromatic acceptor system (quinoid).

Among the different methods of determining excited state dipole moment, solvatochromic correlation method is the most widely used one [7–10]. This method has been based on a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function. The most used solvent polarity functions are those obtained by Lippert–Mataga [11], Bakhshiev [12], Kawski–Chamma–Viallet [13,14]. By using multi-parameter analyses, the solvatochromic data can be also used for quantitative estimation of different types of solute–solvent interactions [15]. The multi-parameter analyses characterize, independently, the extent and type of solute–solvent interactions in ground, transition, and excited states [16].

In spite of significant reports on the optical properties of NR, investigation of ground- and excited-state dipole moments in anisotropic media is still an important problem, where, liquid crystals are excellent media for investigation of anisotropic interactions [17]. The study reported here is concerned with the observation and comparison of the ground- and excited-state dipole moments of NR in liquid and liquid crystalline solvents. Moreover, this work is characterized by detailed quantitative studies on the nature and extent of solvent–solute interactions using correlations with multi-parameter solvent polarity scales.

2. Theoretical background

The electric dipole moment of a polar solute polarizes the solvent so that the solute itself experiences an electric field, the reaction field, which is proportional to the solute dipole moment in the ground and excited states. Such proportionalities for the difference and sum of absorption, $\tilde{\nu}_a$, and fluorescence, $\tilde{\nu}_f$, maxima (in cm^{-1}) have been defined by following equations:

$$\tilde{\nu}_a - \tilde{\nu}_f = m\ F_{\mathrm{Lippert-Mataga}}(\varepsilon, n) + \mathrm{constant} \quad (1)$$

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$$\tilde{\nu}_a - \tilde{\nu}_f = m_1 \; F_{\text{Bakhshiev}}(\varepsilon, n) + \text{constant} \tag{2}$$

$$\left(\tilde{\nu}_a + \tilde{\nu}_f\right)\Big/2 = m_2 \; F_{\text{Kawski–Chamma–Viallet}}(\varepsilon, n) + \; \text{constant} \tag{3}$$

where

$$m = 2\left(\mu_e - \mu_g\right)^2 / hca_o^3 \tag{4}$$

$$m_1 = 2\left(\mu_e - \mu_g\right)^2 / hca_o^3 \tag{5}$$

$$m_2 = 2\left(\mu_e^2 - \mu_g^2\right) / hca_o^3 \tag{6}$$

The symbols h and c are Planck's constant and the velocity of light in vacuum, respectively. $F_{\text{Lippert–Mataga}}$ [11], $F_{\text{Bakhshiev}}$ [12], and $F_{\text{Kawski–Chamma–Viallet}}$ [13,14] are solvent polarity functions and are given as:

$$F_{\text{Lippert–Mataga}}(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \tag{7}$$

$$F_{\text{Bakhshiev}}(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \tag{8}$$

$$F_{\text{Kawski–Chamma–Viallet}}(\varepsilon, n) = \left[\frac{2n^2 + 1}{2\left(n^2 + 2\right)}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \frac{3\left(n^4 - 1\right)}{2\left(n^2 + 2\right)^2}\right] \tag{9}$$

The other symbols ε and n are dielectric constant and refractive index of the solvents, respectively. Employing linear curve fitting route for $\tilde{\nu}_a - \tilde{\nu}_f$ versus $F_{\text{Lippert–Mataga}}$, $\tilde{\nu}_a - \tilde{\nu}_f$ versus $F_{\text{Bakhshiev}}$ and $(\tilde{\nu}_a + \tilde{\nu}_f)/2$ versus $F_{\text{Kawski–Chamma–Viallet}}$ gives m, m_1 and m_2, respectively. If it can be supposed that ground- and excited-states dipole moments are parallel, then:

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca_o^3}{2m_1}\right)^{1/2} \tag{10}$$

$$\mu_e = \frac{m_2 + m_1}{2}\left(\frac{hca_o^3}{2m_1}\right)^{1/2} \tag{11}$$

$$\mu_e = \left(\frac{m_2 + m_1}{m_2 - m_1}\right)\mu_g, \left(m_2 > m_1\right) \tag{12}$$

Moreover, the method based on the empirical polarity scale, E_T^N [18], can be used for estimating dipole variation ($\Delta\mu$) from solvatochromic shift. The theoretical basis for the correlation of the spectral shift with E_T^N has been developed by Ravi et al. [19]:

$$\tilde{\nu}_a - \tilde{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a_o}\right)^3\right]E_T^N + \text{constant} \tag{13}$$

where $\Delta\mu_B = 9\text{D}$ and $a_B = 6.2$ Å are the change in dipole moment on excitation and Onsager radius of reference betaine dye, respectively. $\Delta\mu$ and a_o are the corresponding dipole moment change and Onsager radius for the solute molecule. The change in dipole moment $\Delta\mu$, can be determined as:

$$\Delta\mu = \left(\mu_e - \mu_g\right) = \sqrt{\frac{m_{E_T^N} \times 81}{\left(6.2/a_o\right)^3 \times 11307.6}} \tag{14}$$

where $m_{E_T^N}$ is the slope obtained from the linear plot of Stokes shift $(\tilde{\nu}_a - \tilde{\nu}_f)$ versus microscopic solvent polarity E_T^N.

3. Experimental

Nile red (Fig. 1a) was obtained from Aldrich (laser grade) and used without further purification. All the organic solvents with high purity were purchased from Merck and their physical properties are listed in Table 1.

Six pure nematic liquid crystals were used in our experiments as anisotropic hosts. They are pentyl cyanobiphenyl (5CB), hexyl -cyanobiphenyl (6CB), 4-trans-4-n-hexyl-cyclohexyl-isothiocyanato-benzene (6CHBT), 4-methoxybenzylidene- 4-n-butylaniline (MBBA), 2-chloro-4-heptylphenyl-4-pentylbicyclo [2,2,2] octane-1-carboxylate (7CP5BOC) and the 2-chloro-4-heptylphenyl- 4-heptylbicyclo [2,2,2] octane-1-carboxylate (7CP7BOC). The chemical structures of the pure liquid crystalline materials are shown in Fig. 1b. In this work, the nematic mixtures of 1294-1b and 1751 with high and positive dielectric anisotropy were also used as anisotropic solvents. All the nematic materials, except MBBA, were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland. MBBA was made in our laboratory by a well-known condensation method using distilled n-butylaniline and methoxybenzaldehyde.

The absorption spectra of the dye were recorded on a double beam Shimadzu UV–Visible spectrophotometer (Model UV-2450

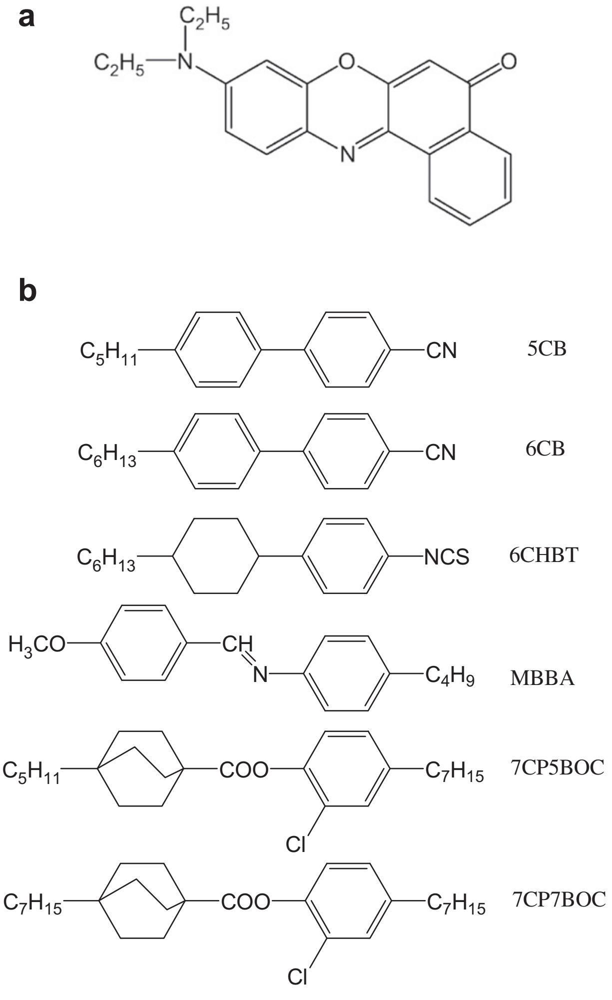

Fig. 1. (a) Structure of NR, (b) the nematic liquid crystals.

Table 1
Spectral parameters of NR in isotropic and anisotropic solvents together with physical properties for the solvents used, taken from Ref. [21].

Solvent	ε	n	$\tilde{\nu}_a$ cm^{-1}	$\tilde{\nu}_f$ cm^{-1}	$F(\varepsilon, n)_L$	$F(\varepsilon, n)_B$	$F(\varepsilon, n)_{K.C.V}$
Isotropic solvent							
n-Heptane	1.92	1.3876	20,533	19,047	−0.0007	−0.0013	0.2629
Cyclohexane	2.02	1.4262	20,366	18,484	−0.0016	−0.0033	0.2876
1,4-Dioxane	2.21	1.4224	19,230	17,152	0.0205	0.0415	0.3074
Tetrachloromethane	2.24	1.4602	19,083	17,985	0.0112	0.0235	0.3233
Toluene	2.38	1.4969	19,083	17,574	0.0132	0.0291	0.3499
Ethyl acetate	6.02	1.3724	19,047	16,806	0.1996	0.4891	0.4979
THF	7.58	1.4072	18,867	16,806	0.2096	0.5491	0.5511
Dichloromethane	8.93	1.4242	18,484	16,638	0.2171	0.5903	0.583
1-Butanol	17.40	1.3990	18,261	15,923	0.2633	0.7494	0.6459
Acetone	21.01	1.3590	18,796	16,556	0.2847	0.7925	0.6406
Ethanol	24.30	1.3610	18,181	15,748	0.2886	0.8117	0.6516
Methanol	33.70	1.3290	18,195	15,576	0.3090	0.8575	0.6529
Acetonitrile	35.94	1.3441	18,653	16,260	0.3046	0.8593	0.664
DMF	38.25	1.4300	18,315	16,181	0.2754	0.8395	0.7114
DMSO	47.24	1.4790	18,050	15,898	0.2634	0.8414	0.7445
Water	78.40	1.3330	16,920	15,037	0.3199	0.9127	0.6832
Anisotropic solvent							
7CP7BOC	3.40	1.500	18,904	17,483	0.0804	0.1945	0.4346
7CP5BOC	3.50	1.510	18,939	17,391	0.0823	0.2020	0.4448
MBBA	5.20	1.613	19,231	16,892	0.1102	0.3171	0.5672
6CHBT	6.80	1.570	18,797	17,331	0.1502	0.4396	0.6017
6CB	9.80	1.583	18,382	16,722	0.1767	0.5491	0.6646
5CB	10.10	1.587	18,519	16,750	0.1777	0.5558	0.6704
1294-1b[a]	14.00	1.600	18,450	16,863	0.1934	0.6313	0.7163
1751[a]	21.00	1.560	18,868	16,920	0.2208	0.7228	0.7370

[a] Nematic mixture.

Scan). Fluorescence of the dye solutions were studied with a JASCO FP-6200 with standard Quartz cuvettes. The dye concentrations were chosen to be about 1×10^{-5} M for all the liquid solutions. The uncertainties in the measured wavelength of absorption and emission maxima are ±0.1 nm and ±1 nm, respectively. The liquid crystal cells were made by sandwiching the nematic solutions between two optical quartz plates (2×1.2 cm^2). The spacing between the cell's surfaces was 50 μm. The introduction of the dye-doped liquid crystal was achieved by capillary action. The dye was studied in the nematic media up to a concentration about 0.2% w/w.

4. Results and discussion

4.1. Absorption and fluorescence spectra of NR

The spectral characteristics of NR in eight nematic hosts as well as several isotropic liquid solvents were investigated. Some spectral data are summarized in Table 1.

Typical absorption and emission spectra of the dye in isotropic liquid solvents (dichloromethane and ethanol) are demonstrated in Fig. 2a. Both the absorption and emission bands split in non-polar solvents, but such splitting does not occur in polar solvents. Consequently, the locations of maximum for absorption and emission bands were determined by fitting the spectra into several Gaussian bands.

4.2. Solvatochromic behavior of NR in anisotropic media

The spectral data together with selected physical properties of the nematic compounds used in this work are summarized in Table 1. The mean dielectric constant $\overline{\varepsilon}$, and refractive index $\overline{n}$, in the nematic phase were calculated using well-known relations [5]. As it can be seen, the dye molecules experience a wide range of polarity and polarizability in anisotropic media. Therefore, in this investigation we might be able to determine the role of dipolar and or dispersive interactions between the dye and the nematic molecules.

Typical NR absorption and fluorescence spectra in the nematic media are shown in Fig. 2b. The band characteristic of the dye in the nematic mixtures might be due to the different molecular interactions between the dye molecule and the components used in the nematic mixtures. As it is evident, from Table 1, the spectral data does not show a regular variation on going from low polar to polar anisotropic solvents. However, similar to polar ordinary solvents, NR shows only single absorption and emission bands in anisotropic media.

4.3. Correlation with multi-parameter solvent polarity scale

In order to characterize the effect of solvent on spectral features of the dye, Kamlet–Abboud–Taft (KAT) and Katritzky (KTZ) multi-parameter solvent polarity scales were used [16]. These polarity scales were applied as:

$$A = A_o + a \cdot E_T(30) + b \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c \cdot \left(\frac{n^2 - 1}{2n^2 + 1}\right) \tag{15.a}$$

$$A = A_o + a' \cdot \alpha + b' \cdot \beta + c' \cdot \pi^* \tag{15.b}$$

A is the solute property (such as $\tilde{\nu}_a$,$\tilde{\nu}_f$ and $\tilde{\nu}_a - \tilde{\nu}_f$) and the coefficients a, a', b, b' and c, c' measure the relative susceptibilities of this property to the indicated solvent features. Katritzky et al. combined successfully Reichardt polarity function ($E_T(30)$) with the dielectric constant and index of refraction functions as a multi-parameter polarity scale. The KAT equation [18] combines spectroscopic polarity scales including hydrogen bonding donor ability (α), hydrogen bonding accepting ability (β) and dipolarity/polarizability (π^*), as a multi-parameter scale.

For KTZ equation, in order to have a comparable coefficients (i.e. a', b' and c'), we have re-normalized and re-scaled the parameters for all the employed solvents. For both the multi-parameter analyses, using the data quoted in Table 1 and multi-linear regression analysis, the results were obtained (Table 2). The results for the liquid solvents were changed as percentage contributions and were summarized in Table 3.

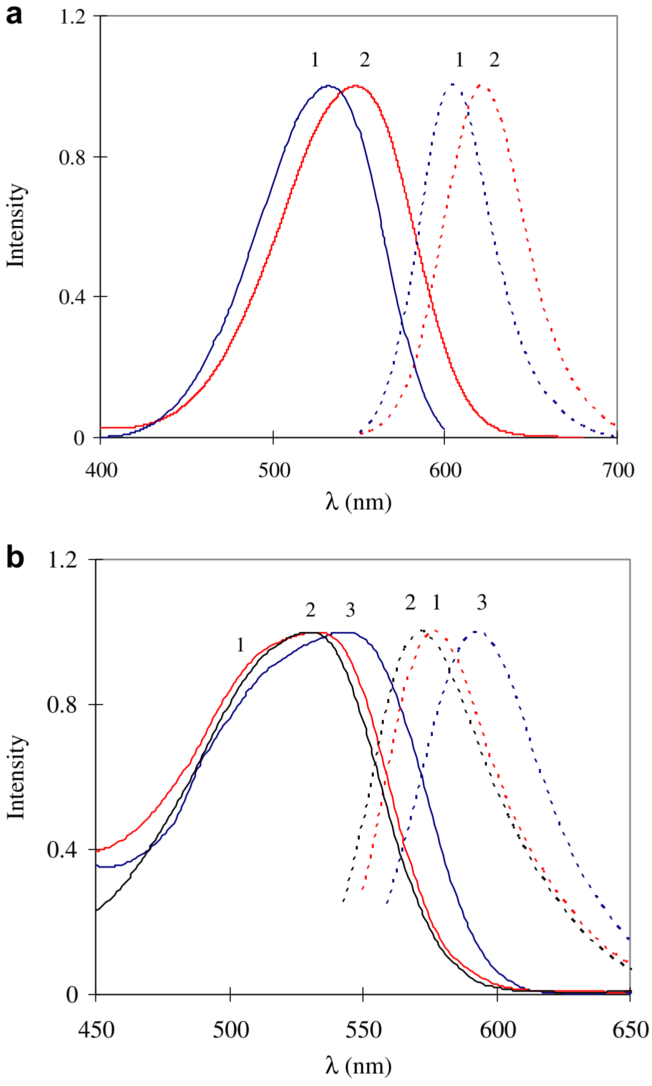

Fig. 2. Absorption and emission spectra of NR in (a) isotropic solvents; (1) dichloromethane, (2) ethanol, and (b) in anisotropic solvents; (1) 6CHBT, (2) 7CP5BOC, (3) 1294-1b.

It was found that selected set of solvents gives results that are more reliable. First, we used all the solvents in multi-parameter analysis, and then according to statistical factors (larger coefficient of determination and smaller values for significance of F-test) and visual inspection we removed inappropriate data and selected the maximum number of data that satisfy the statistical criteria. In this way, the isotropic solvents were selected according to the nature of intermolecular interactions rather than bulk solvent properties. It should be noted that, investigation of the absorption and emission, separately, provides quantitative information that is more valuable. Investigation of absorption data gives information on the molecule in ground and Franck–Condon excited state. While investigation of emission data provides information on the molecule in excited state and in Franck–Condon ground state. Moreover, such analysis on Stokes shift data offers information on solvent reorientation process [18].

Tables 2 and 3 show that in KTZ correlation, the value connected with $E_T(30)$ has the major effectiveness. While the KAT correlation for the same data reveals that π^* has dominant contribution. Apparently, it might be considered as contradiction. However, it can be realized, because $E_T(30)$ parameter is a universal polarity scale that includes contributions from dipolarity and polarizability. It should be noted that comparing the absolute coefficients from different multi-parameter scales is not dependable. The appropriate approach is exploring variations of different parameter contributions from the same model.

Tables 2 and 3 show, going from ground state to excited state, dipolarity and polarizability contributions decrease while specific interaction contributions, and particularly β contribution, increases. It is obvious that in both ground and excited states the major contributions are provided through polar and dispersive interactions. However, there is an interesting distinction in specific interaction contributions into ground and excited states. Generally, the α contributions are similar for both the states. In contrast, β contribution into excited state unexpectedly increases as compared to ground state.

Analyses of Stokes shift data, using KAT and KTZ multi-parameter polarity scales, confirm the same contributions in solvent reorientation processes. It means that the solvent molecules reorient in such a way that support change of intermolecular interactions. However, such correlations have been made with fewer numbers of data and therefore this conclusion should be generalized carefully.

For both the KAT and KTZ correlations, coefficients connected with specific interactions are significant. It denotes that the specific interaction contribution cannot be neglected. Still, we decided to employ KAT approach for anisotropic set, i.e. neglecting specific interactions contribution; however, the results prove importance of specific interactions contribution. The weak correlations, which obtain for a few numbers of data, imply that specific interactions (e.g. anisotropic interactions, extra π–π interaction, and H-bonding) play important role in solublization of NR in liquid crystalline media.

Table 2
Multi-linear regression results for KAT and KTZ multi-parameter scales.

Multi–parameter scale	Spectral feature[a]		Intercept	a, a' (cm^{-1})	b, b' (cm^{-1})	c, c' (cm^{-1})	R^2	Prob. >F
Katritzky	Isotropic solvents	Absorbance (12)	23029.42 (±556.83)	−2079.81 (±400.39)	−575.75 (±301.76)	−622.68 (±215.47)	0.957	<0.0001
		Fluorescence (12)	20539.37 (±423.06)	−2347.23 (±289.80)	−271.81 (±219.46)	−397.26 (±165.48)	0.974	<0.0001
		Stokes shift (9)	2326.12 (±444.49)	651.94 (±113.06)	−243.2 (±242.24)	−520.93 (±165.63)	0.975	0.0002
	Liquid crystals	Absorbance (5)	18925.47 (±55.67)	–	−808.17 (±385.43)	−26.91 (±246.24)	0.949	0.0512
		Fluorescence (6)	17452.6 (±78.96)	–	−230.43 (±131)	−590.59 (±124.17)	0.926	0.0201
		Stokes shift (5)	1439.31 (±163.37)	–	29.79 (±274.05)	746.08 (±268.73)	0.812	0.1876
KAT[b]	Isotropic solvents	Absorbance (13)	20301.16 (±57.98)	−792.87 (±72.52)	−114.99 (±140.48)	−2234.71 (±114.67)	0.992	<0.0001
		Fluorescence (12)	18413.06 (±95.59)	−898.11 (±112.14)	−1098.21 (±181.39)	−1763.8 (±165.65)	0.985	<0.0001
		Stokes shift (8)	1484.11 (±64.02)	64.31 (±65.17)	1186.55 (±122.66)	−204.03 (±99.48)	0.970	0.0017

[a] Number in parentheses denotes the number of data points used in correlation.
[b] Kamlet–Abboud–Taft.

Table 3
Percentage of different parameters contributions for KAT and KTZ multi-parameter scales.

Multi-parameter scale	Spectral feature	P_{ε_r} (%)	P_n (%)	$P_{E_T(30)}$ (%)	
		P_{π^*} (%)		P_α (%)	P_β (%)
Katritzky	Absorbance	18 (±9)	19 (±7)	63 (±12)	
Kamlet–Abboud–Taft		71 (±4)		25 (±2)	4 (±4)
Katritzky	Fluorescence	9 (±7)	13 (±5)	78 (±10)	
Kamlet–Abboud–Taft		47 (±4)		24 (±3)	29 (±5)
Katritzky	Stokes shift	7 (±15)	54 (±3)	39 (±15)	
Kamlet–Abboud–Taft		14 (±7)		4 (±4)	82 (±8)

4.4. Evaluation of the dipole moments

In dipole estimation, proper selected sets of solvents, which provide the best fit for the correlations, were used (Eqs. (1)–(3) and (13)). Onsager cavity with radius of 4.1 Å has been evaluated for NR dipole estimation [8]. The calculated ground- and excited-states dipole moments in liquid and liquid crystalline media are summarized in Table 4. Typical data correlated with solvent polarity functions are also illustrated in Fig. 3.

As it can be seen, the estimated dipole values are not consistent and comparable. It can be explained that for fair results, both the used polarity functions should have acceptable correlation coefficients, simultaneously. In this way, Kawski–Chamma–Viallet function and microscopic solvent polarity scale E_T^N, exhibit reliable correlation coefficients. The obtained values for the ground state dipole moment (i.e. 7.97D and 7.51D) are completely acceptable and are in agreement with previously reported values [2,8].

However, the value of 7.97D for ground state dipole moment was used for calculation of the excited state dipole moment. This value is close to that of the previously reported value (i.e. $\mu_g \cong 8D$) [20]. The results, which are more consistent and comparable, are summarized in Table 5. As it can be seen, larger excited state dipole moments for NR were obtained in both the isotropic and anisotropic media.

The negative charge on the terminal oxygen atom of the possible resonance structure favors the proposed delocalization [5]. The resonance structure suggests that the excited state is intramolecular charge transfer in nature. In excited state, the tilted diethylamino group attached to the dye aromatic skeleton increases structural planarity. This structural reconfiguration enhances dispersion force contribution into solvent reorientation process as it was predicted from Stokes shift data, correlated by KAT multi-parameter scale.

In addition, the result for microscopic polarity scale E_T^N, shows a large dipole moment change ($\Delta\mu = 5.18D$) that indicates importance of general type of solute–solvent interactions as well as H-bonding interactions. The excited state dipole moment values estimated by other polarity functions are acceptable and in agreement with previously reported values. The differences observed between the excited state dipole moment values are reasonable, as the polarity functions essentially evaluate the dipolar interactions. Moreover, it can also be explained in terms of different theoretical

Table 4
Calculated ground- and excited-state dipole moments (μ_g and μ_e) in selected isotropic and anisotropic solvents.

Medium	Polarity function[a]	Slope	R^2	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_e/μ_g
Isotropic solvents	E_T^N (8)	871.90	0.95	7.51[b]	12.69	5.18	1.69
	Lippert–Mataga (8)	2970.56	0.96	1.69	6.20	4.51	3.67
	Bakshiev (8)	1142.27	0.96	5.46	8.26	2.80	1.51
	Kawski–Chamma–Viallet (8)	−6938.28	0.97	7.97[b]	10.07[b]	2.01	1.26
Liquid crystals	Lippert–Mataga (5)	2999.06	0.87	1.00	3.53	2.53	3.53
	Bakshiev (5)	805.45	0.88	1.27	3.62	2.35	2.85
	Kawski–Chamma–Viallet (5)	−2231.61	0.94	3.49	5.24	1.75	1.50

[a] Number in parentheses denotes the number of data points used in calculations.
[b] Obtained from Bakhshiev relation as simultaneous equation.

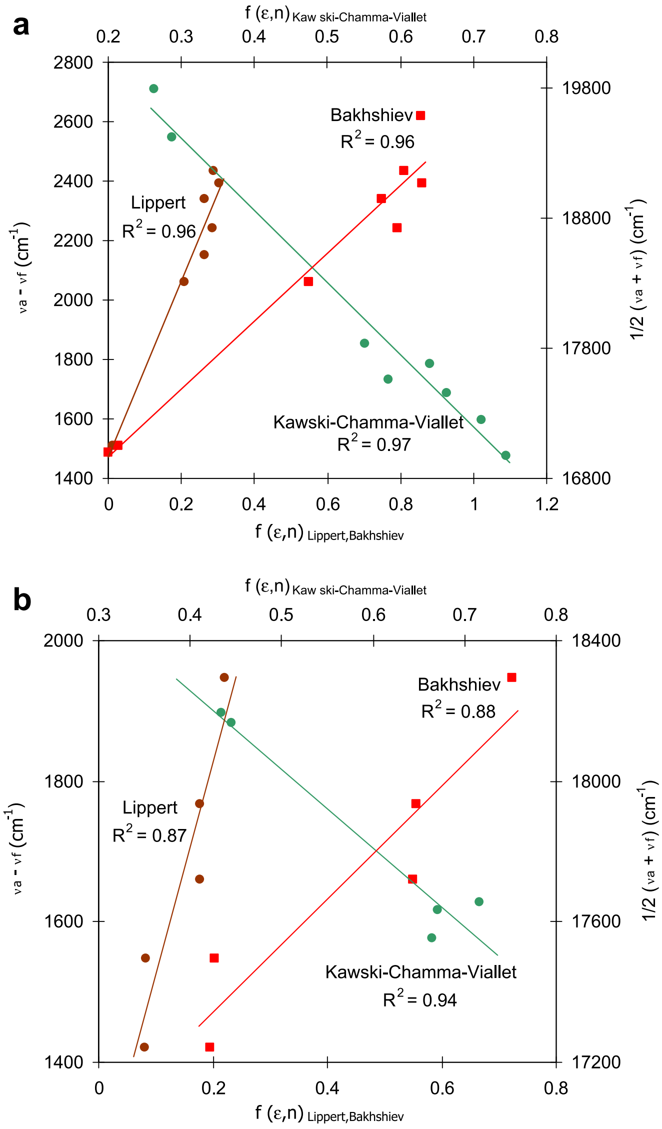

Fig. 3. Solvent polarity functions fitness; (a) NR in selected isotropic solvents, (b) NR in selected anisotropic solvents.

Table 5
Excited state dipole moments (μ_e) in selected isotropic and anisotropic solvents.

Medium	Polarity function[a]	Slope	R^2	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_e/μ_g
Isotropic solvents	E_T^N (8)	871.90	0.95	7.97	13.15	5.18	1.65
	Lippert–Mataga (8)	2970.56	0.96		12.48	4.51	1.57
	Bakshiev (8)	1142.27	0.96		10.77	2.80	1.35
	Kawski–Chamma–Viallet (8)	−6938.28	0.97		14.13	6.16	1.77
Liquid crystals	Lippert–Mataga (5)	2999.06	0.87		12.50	4.53	1.57
	Bakshiev (5)	805.45	0.88		10.32	2.35	1.29
	Kawski–Chamma–Viallet (5)	−2231.61	0.94		12.11	3.91	1.49

[a] Number in parentheses denotes the number of data points used in calculations.

considerations employed in the development of these polarity functions.

Along with investigation in ordinary solvents, this report is mainly concerned with the quantitative study of the anisotropic solvent effect on the spectral behavior of NR. As it has been mentioned in our recent publication [21], the main barrier seems to be theoretical background that approximates the solvent medium as a homogeneous and isotropic dielectric continuum. Nematic liquid crystals are anisotropic in nature; however, in microscopic scales they can be estimated as isotropic media [21–23]. Consequently, it motivated us to investigate applicability of the solvatochromic method in a series of anisotropic nematic compounds. It was found that adequate correlation could be established for selected liquid crystalline set. The data in Table 5 show that despite of weak correlations for few numbers of data, the estimated excited state dipole moments are reliable and comparable to those in isotropic media. These results show that solvatochromic method, even with the restrictions, is applicable for anisotropic media.

NR structural characteristic makes it able to interact with the media through different combination of specific/non-specific interactions. The obtained results from KAT and KTZ multiparameter analysis and dipole moment variation demonstrate that NR dipole moment increases during the transition to Frank-Condon excited state. Then the solvent molecules reorient so that they can provide better contribution into the dye stabilization through dispersive and specific interactions, particularly hydrogen bond accepting. This stabilization guides the dye to relaxed excited state where the dye emits light and then goes to Franck–Condon ground state. After that through another solvent reorientation process, it goes to relaxed ground state where the solvent mainly interact through dipolar and specific interactions, particularly hydrogen bond donating.

NR is able to accept H-bonds but it is very weak H-bond donor. At this point, a question arises. How hydrogen bonding acceptor ability of the solvent has the main contribution on the dye stabilization during excitation? It might be explained in terms of solvent–solvent interactions. In ground state both amino and carbonyl groups of the dye act as hydrogen bond acceptor sites. During excitation, the internal charge transfer make the amino group hydrogen bond acceptor ability vanished. Therefore, the solvent ability to take away the hydrogen bond donor groups from this positively charged site plays essential role in stabilization of the dye.

Since spectroscopic polarity parameters are not available for the liquid crystals, detailed interpretation of the interactions in the liquid crystalline media cannot be provided. However, similarity of the dipole variation in both the isotropic and anisotropic media and the limited KTZ analysis concludes that, dispersive and specific interactions are effective interactions in NR solublization into the liquid crystalline media.

5. Conclusion

The absorption and emission spectra of NR in liquid and liquid crystalline media were studied. The solvatochromic method was used to determine the ground- and excited-state dipole moments. It was shown that the excited state dipole moment is about 4.5D larger than that of the ground state dipole moment (7.97D). It may arise from relatively large dipole moment change due to intramolecular charge transfer and resonance structure contribution. Moreover, applicability of solvatochromic method for NR in anisotropic media was investigated. The results suggest that solvatochromic method is reliable for investigation of simple neutral dyes in anisotropic media. The dipole moment variation within KAT and KTZ analyses show that dispersive and specific interactions are the most effective parameters on optical behavior of the dye in the isotropic and anisotropic media.

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