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Solvent polarity scale on the fluorescence spectra of a dansyl monomer copolymerizable in aqueous media

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Abstract

A copolymerizable fluorescent monomer N-[2-[[[5-(N,N-dimethylamino)-1-naphthalenyl]sulfonyl]-amino]ethyl]-2propenamide (DANSAEP) was synthesized, which exhibits dual fluorescence due to the twisted intramolecular charge transfer in the excited state. The emission maximum λ_{em} shifts from 463.3 nm in *n*-hexane to 530.0 nm in water, showing solvent polarity dependence. The relations between λ_{em} and the conventional solvent polarity parameters $E_T(30)$ or Z are linear, dividing solvents into protic and aprotic groups. Kamlet's linear solvation energy relationship gives a good description for λ_{em} as a solvent polarity scale. The increment of dipole moment $\Delta \mu$ at the excited state was estimated as 5.09 D with the solvatochromic analysis. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The finding of volume phase transition in gels raises an important question on the solvation behavior of polyelectrolytes, since all gels showing discontinuous volume phase transition in response to infinitesimal stimulation usually contain more or less ionizable groups on the chains [1]. For highly charged strong polyelectrolytes in mixed organic solvents, the composition of solvent at which the volume phase transition occurs in crosslinked gel is found to be similar to that inducing the corresponding linear polyelectrolyte to precipitate from the homogeneous solution [2-6]. This fact implies that the macroscopic volume phase transition and precipitation appear to be caused by the change in the solvation of the macromolecular chains, which alters the intra-

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and intermolecular interactions and chain conformation. Fluorescence of polyelectrolyte is expected to be able to reveal the changing pattern of the polarity in the solvation layer.

Fluorescence label techniques have been widely used in polymer research [7,8]. For our purpose, the label should be easy to copolymerize with ionic monomers in aqueous media and definitely represent the polarity change around the chromophore. Pyrene and dansyl probes are most desirable candidates [8–10]. The pyrene scale for the solvent polarity is well established on the relative intensity I_1/I_3 [9]. However, this probe exhibits a strong tendency to form exciplexes in water at relatively low concentration [8], which limits its application in polyelectrolyte. The emission maximum of dansyl groups covalently linked to polymer shifts with solvent polarity [7,10,11]. A universal relation between the emission maximum of our dansyl monomer and the

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medium polarity is required to interpret the polyelectrolyte solvation in mixed solvents.

Several empirical solvent polarity parameters have been proposed to characterize and rank the polarity of solvent [12]. Among the more well known are Dimroth's $E_{\rm T}(30)$ [13,14] and Kosower's Z scales [15–17]. Both are based on the transition energy of specified compounds excited in objective solvent. Moreover, the Kamlet–Taft linear solvation energy relationship (LSER) [12,18–20] containing multiple solvatochromic parameters for individual interaction has been successfully utilized in quantitative structure-property/activity relationships study.

To follow the polarity change in the solvation layer of polyelectrolytes, we synthesized a dansyl monomer, N-[2-[[[5-(N,N-dimethylamino)-1-naphthaleny1]sulfony1]-amino]ethy1]-2-propenamide (DANSAEP) (Scheme 1). The relationship between the observed emission maximum and solvent polarity parameters was established from less-polar hexane to water.

2. Experimental

2.1. Materials

Dansyl chloride, acryloyl chloride (Aldrich), and other reagents were all from commercial sources and were further purified just before use according to standard procedure [21]. All reactions were performed under the nitrogen atmosphere.

2.2. Preparation of N-(2-aminoethyl)-5-(dimethylamino)-naphthalene sulfonamide [22] (DANSA)

To a solution of ethylenediamine (2.18 ml, 32.24 mmol) in THF (150 ml) at 0°C was added dropwise dansyl chloride (0.8875 g, 3.224 mmol) in THF (100 ml). The reaction was stirred at 0°C for 4 h, and 1 N KOH (9 ml) was added. The THF was evaporated,

and the aqueous layer was extracted with CH_2Cl_2 (4 × 50 ml). The combined organic layer was dried with MgSO₄ and evaporated to leave pale yellowgreen oil. Crystallization from ethanol/water gave light-green needles (0.5653 g, mp 149–151°C, yield 60.6%). ¹H-NMR (400 MHz, CDCl₃): δ 8.51 (d, 1 H, *J* = 8.4 Hz, ArH); 8.29 (d, 1 H, *J* = 8.4 Hz, ArH); 8.22 (d, 1 H, *J* = 8.4 Hz, ArH); 7.51 (m, 2 H, ArH); 7.15 (d, 1 H, *J* = 7.6 Hz, ArH); 2.90 (m, 8 H, N(CH₃)₂ and SO₂NHCH₂); and 2.68 (m, 2 H, CH₂NH₂).

2.3. Preparation of N-[2-[[[5-(N,N-dimethylamino)-1-naphthalenyl]sulfonyl]-amino]ethyl]-2-propenamide [22] (DANSAEP)

To a solution of DANSA (0.3007 g, 1.04 mmol) in THF (30 ml) at room temperature was added acryloyl chloride (0.085 ml, 1.04 mmol) and triethylamine (0.145 ml, 1.04 mmol). The reaction was stirred at room temperature overnight. The salts were then filtered and washed with THF. The combined filtrates were evaporated, and the residue was chromatographed on silica with ether/hexane (4/1) as eluent to give light-green solid or needle DANSAEP (0.2790 g, m.p. 105–107°C, yield 78.2%). ¹H-NMR (400 MHz, CDCl₂): δ 8.50 (d, 1 H, J = 8.4 Hz, ArH); 8.25 (d 1 H, J = 8.8 Hz, ArH); 8.18 (d, 1 H, J = 7.2 Hz, ArH); 7.47 (m, 2 H, ArH); 7.13 (d, 1 H, J = 7.2 Hz, ArH); 6.60 (br, 1 H, CONH); 6.25 (br, 1 H, SO₂NH); 6.12 (d, 1 H, J = 17.2 Hz, vinyl); 5.88 (dd, 1 H, J = 10 and 17 Hz, vinyl); 5.48 (d, 1 H, J = 10 Hz, vinyl); 3.35 (m, 2 H, COCNCH₂); 3.03 $(m, 2 H, SO_2 NHCH_2)$; and 2.84 $(s, 6 H, N(CH_2)_2)$. ¹³C-NMR (400 MHz, CDCl₃): δ 166.3, 151.8, 134.2, 130.5, 130.3, 129.7, 129.4, 129.3, 128.4, 126.5, 123.1, 118.6, 115.2, 45.3, 42.8, 39.2,

2.4. Spectral measurements

Fluorescence spectra of DANSAEP were recorded in 12 solvents at concentration of 1×10^{-5} mol/l at room temperature with a Perkin-Elmer LS50B Luminescence spectrometer, using an excitation wavelength of 330 nm. UV absorption spectra were measured with a Hitachi UV-240 spectrophotometer. ¹Hand ¹³C-NMR was recorded on a Bruker DRX-400 spectrometer.

3. Results and discussion

3.1. Absorption spectra and fluorescence spectra

The absorption and fluorescence spectra of DANSAEP in several select solvents are illustrated as examples in Fig. 1. There appear three absorption bands in the UV spectra, being identical for all the solutions. In most solvents the DANSAEP exhibits



Fig. 1. Absorption spectra (a) and fluorescent spectra (b) of DANSAEP at room temperature in solvents indicated by numbers as the same as those in Table 1.

dual fluorescence: One at high energy (b^* band) is from the non-charge-transfer state and the other at low energy (a^* band) from the twisted intramolecular charge-transfer (TICT) state, in which the dimethylamino group plane is nearly perpendicular to naphthalene plane [23,24]. The relative intensity of a^* and b^* emission bands varies with the solvent polarity due to the different quantum yields. In so dilute solutions, the intensity of two bands varies with the chromophore concentration without any change in the band position.

We summarize the absorption λ_{abs} and fluorescence maximum λ_{em} (a^{*} band) of DANSAEP in 12 tested solvents in Table 1 with solvent bulk properties. One can find that the lowest energy absorption band λ_{abs} is almost constant in 12 solvents while the emission maximum λ_{em} obviously varies with solvents. According to the TICT hypothesis [23,24] the wavelength of a^{*} band is sensitive to the local polarity of the medium. In water the emission maximum λ_{em} of DANSAEP is 530 nm and in less-polar *n*-hexane λ_{em} is blue-shifted to ~ 460 nm. The fact suggests that λ_{em} can be used as a polarity scale for characterizing solvents. In Section 3.2 we will demonstrate the establishment of relations between λ_{em} and solvent polarity parameters.

There may be an argument on λ_{em} of dansyl and its derivatives. Shea et al. [26] reported that for 5-(dimethylamino)-1-[[[p(m)-vinyl benzyl]amino]sulfonyl]naphthalene $\lambda_{\rm em}$ is 453.9 nm in *n*-hexane and 537.8 nm in water. Strauss and Vernewe [10] observed that the λ_{em} of 580 nm for 1-dimethylamino-5-(β-aminoethyl)sulfonamidonaphthalene in water was blue-shifted to 520 nm when the probe was conjugated with the butyl polyacid. The substituent to the chromophore alters its solvation, which in turn changes the energy of excited states. Seliskar and Brand [27] found that λ_{em} varied from 414 to 544 nm for a variety of substituted 2-aminonaphthalenes in water. These results indicate that each of these dansyl molecules should be treated as an independent polarity scale.

3.2. The dansyl scale of solvent polarity

In order to build the dansyl scale of DANSAEP for ranking the solvent polarity, we correlate the λ_{em} with some effective solvent polarity parameters. The

Table 1

Refractive index *n*, dielectric constant ε , Dimroth's $E_{\rm T}(30)$, Kosower's Z, the absorption $\lambda_{\rm abs}$ and fluorescence maximum $\lambda_{\rm em}$ of DANSAEP in tested solvents at room temperature

No.	Solvent	n ^a	ε^{a}	$E_{\rm T}(30)^{\rm b}$ (J mol ⁻¹)	Z^{c}	λ_{abs} (nm)	$\lambda_{\rm em}$ (nm)
1	<i>n</i> -hexane	1.372	1.89	129.3	_	333.7	463
2	diethyl ether	1.35	4.20	144.8	-	332.5	478.5
3	benzene	1.498	2.27	144.4	_	_	483
4	dioxane	1.420	2.21	150.6	-	336.7	488.5
5	tetrahydrofuran	1.405	7.58	156.5	_	335.7	489.5
6	dichloromethane	1.421	8.93	172.0	64.2	337.8	496
7	acetone	1.356	20.56	176.6	65.7	336.5	498.5
8	ethanol	1.359	24.55	217.2	79.6	334.9	506.5
9	dimethylformamide	1.428	36.71	183.3	68.5	337.3	505.6
10	methanol	1.327	32.66	232.3	83.6	336.3	512
11	dimethyl sulfoxide	1.477	46.45	188.3	71.1	-	515
12	water	1.333	78.30	264.3	94.6	329.3	530.0

^aFrom Refs. [21,25].

^bFrom Ref. [13].

^c From Refs. [15,16].

first attempt is based on the $E_{\rm T}(30)$, which is defined as the transition energy of the intramolecular charge-transfer band of pyridinium-N-phenolbetaine [13,14]. Fig. 2 presents the plot of $\lambda_{\rm em}$ against $E_{\rm T}(30)$ listed in the fifth column of Table 1. We can see that the data are divided into two groups, one for aprotic solvents with $E_{\rm T}(30)$ values lower than 200 J mol⁻¹, the other for protic solvents of ethanol, methanol, and water. Within each group, $\lambda_{\rm em}$ increases linearly with $E_{\rm T}(30)$. These results mean that



Fig. 2. Plot of fluorescence emission maximum λ_{em} against Dimroth's $E_{\rm T}(30)$ for DANSAEP probe in tested solvents (solid lines: linear fitting with the equations indicated).

beside the solvent polarity and polarizability, the proton donating capability in forming hydrogen bond between the solute and solvent is indispensable for characterizing solvent polarity.

Another empirical solvent polarity parameter we adopted is Kosower's Z obtained from the position of the absorption maximum of 1-ethyl-4-carbomethoxypyridinium oxide [15–17]. The plots of λ_{em} against Z (Fig. 3) also manifest the similar behavior of dual linear dependence as found for $E_{T}(30)$ though



Fig. 3. Plot of fluorescence emission maximum λ_{em} vs. Kosower's Z for DANSAEP probe in tested solvents (solid lines: linear fitting with the equations indicated).



Fig. 4. Plot of the observed emission maximum $\lambda_{\rm em}$ against the $\lambda_{\rm em}^{\rm cal}$ calculated with Eq. (1) for DANSAEP probe in tested solvents numbered as in Table 1 (solid line: the diagonal).

only a few points due to the lack of Z values. Dong and Winnik [28] also reported that the pyrene scale was divided into the similar two groups according to the $E_{\rm T}(30)$ or Z.

In fact, the $E_{\rm T}(30)$ and Z are based on the experimental spectral energy level of specified compounds. Therefore, the above finding addresses that the solvent effect on the DANSAEP is different from that on the compounds for $E_{\rm T}(30)$ and Z, especially in the protic solvents due to the hydrogen bonding.

In view of all contributions to the free energy, the linear solvation energy relationship (LSER) developed by Kamlet, Taft and co-workers [18–20] is adopted to correlate the λ_{em} for our observed data. The resulting regression equation is shown below:

$$\lambda_{\rm em} (\rm nm) = 465.20 - 6.99 V_i / 100 + 40.33 \pi^* + 16.59 \alpha_{\rm m} + 12.07 \beta_{\rm m} , \qquad (1)$$

with a correlation coefficient of $r^2 = 0.9865$ and a standard deviation of s = 2.64. Here, V_i is the intrinsic (van der Waals) molecular volume and represents the free energy required to separate the solvent molecule and provide a suitably configured cavity for the solute molecule. π^* is an index of solvent polarity/polarizability as a measure of the molecular ability to stabilize a neighboring charge or dipole through nonspecific dielectric interactions. α_m and $\beta_{\rm m}$ are the indices of hydrogen bond donor strength and acceptor strength, respectively. The observed $\lambda_{\rm em}$ is plotted against the calculated $\lambda_{\rm em}^{\rm cal}$ in Fig. 4, where the diagonal provides a perfect fitting to the data. Thus, we can conclude that the λ_{em} of DANSAEP can be used as a linear scale to rank the solvent polarity following the LSER procedure.

3.3. Solvatochromic analysis

The intramolecular charge-transfer state can be investigated through the difference in dipole mo-

Table 2 Kamlet–Taft's multiple solvatochromic parameters, Δf , and the Stokes shift Δv of DANSAEP probe in tested solvents at room temperature

No.	Solvent	V_{i}^{a} (×10 ⁻²)	$\pi^{* \ a}$	$\alpha_{ m m}^{~~a}$	$eta_{ m m}$ a	$\Delta f^{\rm b}$	$\frac{\Delta v}{(10^{-3} \text{ cm}^{-1})}$
1	<i>n</i> -hexane	0.648	0	0	0	0.001	8.190
2	diethyl ether	0.505	0.27	0	0.47	0.163	9.177
3	benzene	0.491	0.59	0	0.14	-	-
4	dioxane	0.508	0.55	0	0.37	0.021	9.229
5	tetrahydrofuran	0.455	0.58	0	0.55	0.210	9.359
6	dichloromethane	0.278	0.70	0.10	0.09	0.218	9.442
7	acetone	0.380	0.71	0.09	0.49	0.285	9.658
8	ethanol	0.305	0.54	0.83	0.77	0.290	10.116
9	dimethylformamide	0.381	0.88	0	0.69	0.282	9.869
10	methanol	0.205	0.60	0.93	0.62	0.309	10.204
11	dimethyl sulfoxide	0.451	1.00	0	0.76	-	-
12	water	0.102	1.09	1.17	0.18	0.320	11.499

^aFrom Refs. [12,29] or calculated according to Ref. [29].

^bObtained according to Eq. (3).

ments between the first excited singlet state μ_{es} and the ground state μ_g , i.e., $\Delta \mu = \mu_{es} - \mu_g$. The Stokes shift (Δv) of the excited state can be determined by the solvatochromic analysis proposed by Lippert [29] and Mataga [30] as follows [31]:

$$\Delta v = v_{\rm abs} - v_{\rm em}$$

= $\frac{1}{4\pi\varepsilon_0} \frac{2}{hca^3} |\mu_{\rm es} - \mu_{\rm g}|^2 \Delta f + \text{const.},$ (2)

with

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1},\tag{3}$$

where v_{abs} and v_{em} is the wavenumber of the lowest energy absorption maximum and the fluorescence maximum, respectively. ε_0 and ε are the dielectric constant of vacuum and solvent, respectively. n is the refractive index of the solvent. a the radius of the Onsager cavity for the solute molecule. h and c are Planck's constant and the light velocity, respectively. Using the values in Tables 1 and 2, we plot Δv against Δf in Fig. 5. A reasonable linearity is observed from our data except those of water (No. 12) and dioxane (No. 4). For water the deviation may be attributed to the strong hydrogen bonding interaction which interrupts the reorientation of water molecules around the probe. While for dioxane, a similar phenomenon was also observed by Horng [32], who regarded this as the 'local' solvation effect.

The $\Delta\mu$ can be estimated from the slop of the straight line (6.1743) in Fig. 5 when the Onsager cavity radius *a* is determined. The simplest way is to assume $a^3 = 3V/4\pi$, where *V* is the van der Waals volume of the probe molecule [32] and determined by the simple additivity of the atomic volume [25]. The value of a = 0.353 nm so obtained yields a dipole moment change of $\Delta\mu = 5.19$ D. The other approach is to take *a* as 40% of the long axis of the chromophore part of the DANSAEP molecule [33], giving a = 0.366 nm and $\Delta\mu = 5.48$ D.

These data are close to $\Delta \mu = 5.78$ D for dansylmonoaza-18-crown-6 [34] but quite different from $\Delta \mu = 19$ D for N,N-dimethyl-2-aminonaphthalene-6-sulfonate (2,6-DNS, a = 0.4 nm) [27], the latter was determined from ethanol/water mixtures. In the methodology behind Eq. (2), $\Delta \mu$ is assumed to be independent of the solvent polarity, but in fact λ_{em}



Fig. 5. Plot of the Stokes shift Δv vs. the solvent polarity parameters Δf according to Eq. (2) for DANSAEP probe in solvents numbered as in Table 1 (solid line: linear fitting).

varies with solvents as discussed in Section 3.2. Seliskar and Brand considered that such a large change in $\Delta \mu$ of 2,6-DNS was due to the fact that the solvent relaxation could not occur during the lifetime of the first excited singlet state. They expected the increase in the probability of intersystem crossing and appearance of the triplet state induced by the solvent relaxation. Li et al. [35] argued with experimental results that intersystem crossing was relatively unimportant and the 1-(dimethylamino)-5-naphthalenesulfonate (1,5-DNS, the same as our starting compound) spectrum was much more sensitive to solvent effects than that of 2,6-DNS.

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References

- [1] M. Shibayama, T. Takana, Adv. Polym. Sci. 109 (1993) 1, and references therein.
- [2] Z. Tong, X. Liu, Macromolecules 27 (1994) 844.
- [3] X. Liu, Z. Tong, O. Hu, Macromolecules 28 (1995) 3813.
- [4] X. Lui, Z. Tong, X. Cao, O. Hu, Polymer 37 (1996) 5947.

- [5] X. Lui, O. Hu, Z. Tong, J. Polym. Sci. B: Polym. Phys. 35 (1997) 1433.
- [6] X. Lui, Z. Tong, F. Gao, Polym. Int. 47 (1998) 215.
- [7] T. Torii, T. Yamashita, K. Horie, Biopolymers 34 (1994) 101.
- [8] F.M. Winnik, Chem. Rev. 93 (1993) 587.
- [9] K. Kalyanasundaram, J.K. Thomas, J. Am. Chem. Soc. 99 (1977) 2039.
- [10] U.P. Strauss, G. Vesnaver, J. Phys. Chem. 79 (1975) 2426.
- [11] U.P. Strauss, M.S. Schlesinger, J. Phys. Chem. 82 (1978) 1627.
- [12] M. Kamlet, Prog. Phys. Org. Chem. 13 (1982) 485, and references therein.
- [13] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, Liebigs Ann. Chem. 661 (1963) 1.
- [14] K. Dimroth, C. Reichardt, Liebigs Ann. Chem. 727 (1969) 93.
- [15] E.M. Kosower, J. Am. Chem. Soc. 30 (1958) 3253.
- [16] E.M. Kosower, J. Am. Chem. Soc. 30 (1958) 3261.
- [17] E.M. Kosower, J. Am. Chem. Soc. 30 (1958) 3267.
- [18] M.J. Kamlet, J.L. Abboud, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 6027.
- [19] M.J. Kamlet, J.L. Abboud, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 8325.
- [20] M.J. Kamlet, T.N. Hall, J. Boykin, R.W. Taft, J. Chem. Soc. Perkin Trans. 2 (1979) 2559.

- [21] N. Chen, S. Hu, Solvent Handbook, Chemical Engineering Press, Beijing, 1987 (in Chinese).
- [22] K.J. Shea, G.J. Stoddard, D.M. Shavelle, F. Wakui, R.M. Choate, Macromolecules 23 (1990) 449.
- [23] K. Rotkiewicz, K. Grellmann, Z.R. Grabowski, Chem. Phys. Lett. 19 (1973) 315.
- [24] Z.R. Grabowski, K. Rotkiewicz, A. Seimiarczuk, D.J. Cowlev, W. Baumann, Nouv. J. Chim. 3 (1979) 443.
- [25] J.P. Hickey, D.R. Passino-Reader, Environ. Sci. Technol. 25 (1991) 1753.
- [26] K.J. Shea, D.Y. Sasaki, G.J. Stoddard, Macromolecules 22 (1989) 1722.
- [27] C.J. Seliskar, L. Brand, J. Am. Chem. Soc. 93 (1971) 5414.
- [28] D.C. Dong, M.A. Winnik, Can. J. Chem. 62 (1984) 2560.
- [29] E. Lippert, Z. Naturforsch. A 10 (1955) 541.
- [30] N. Mataga, Bull. Chem. Soc. Jpn. 36 (1963) 654.
- [31] Y.V. Il'Ichev, W. Kuhnle, K.A. Zachariasse, Chem. Phys. 211 (1996) 441.
- [32] M.L. Horng, J.A. Gardecki, A. Papazyan, M. Maroncelli, J. Phys. Chem. 99 (1995) 17311.
- [33] J.F. Letard, R. Lapouyade, W. Rettig, Pure Appl. Chem. 65 (1993) 1705.
- [34] Y. Wu, L. Li, A. Tong, Chin. Sci. Tech. Lett. 4 (1998) 196, in Chinese.
- [35] Y.-H. Li, L.-M. Chan, L. Tyer, R.T. Moody, C.M. Himel, D.M. Hercules, J. Am. Chem. Soc. 97 (1975) 3118.