

SOLVATOCHROMIC EFFECTS IN THE FLUORESCENCE OF 2-AMINOANTHRACENE AND *N,N*-DIMETHYL-2-AMINOANTHRACENE: A COMPARATIVE STUDY

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Summary

A comparative study of solvatochromic effects on the fluorescence maxima of 2-aminoanthracene and *N,N*-dimethyl-2-aminoanthracene confirms (i) that the former is affected by solvent-donor hydrogen bonding in hydroxylic solvents and (ii) that the Bilot-Kawski and related expressions of polarizability provide a more specific analysis of solvatochromic effects than the Dimroth parameter and related solvent parameters.

1. Introduction

Solvatochromism, *i.e.* solvent-induced changes in absorption and especially emission spectra, provides the simplest and best-established probe of the change in electron distribution on excitation to the S_1 state, and hence is a method of evaluating the dipole moment of the S_1 state. The topic has been thoroughly reviewed [1 - 4] and while the accuracy of the method must be viewed cautiously, under carefully chosen conditions satisfactory results can be obtained [5 - 7]. The key step involves relating the observed solvatochromism to one or more solvent parameters, and Koutek [7] has evaluated statistically 16 equations based on existing theories of long-range solvent-solute interaction which correlate energies of absorption and fluorescence with such macroscopic solvent properties as refractive index and dielectric constant; he concluded that the near-equivalent approaches of Bilot and Kawski, and of Bakhshiev, afforded optimum results. However, all the treatments agree on certain essentials, *i.e.* (i) the increase of the Stokes shift with solvent polarity results from an increase in the dipole moment of S_1 above that of the S_0 state; (ii) fluorescence from unsubstituted aromatic hydrocarbons (ArH) shows little sensitivity to the solvent because of the high symmetries of both S_0 and S_1 states [8]; (iii) substitution of ArH by good electron donor or acceptor groups will induce large solvatochromic effects in fluorescence because of an increase in intramolecular charge transfer in the S_1 state [9].

An alternative approach to the problem is the use of empirically- or theoretically-derived solvent parameters, taken as accurate registers of solvent polarity, in correlating molecular spectroscopic properties [10 - 13]. For the prediction of fluorescence maxima, the most successful parameters are the $E_T(30)$ parameter, also known as the Dimroth parameter or the Reichardt-Dimroth parameter [14, 15], and the Z parameter of Kosower [10 - 13, 16], both of which are based on the high solvent sensitivity of charge transfer absorptions in pyridinium phenol betaine and pyridinium iodide respectively. One shortcoming of these scales is that they incorporate both hydrogen bonding effects and solvent polarity in the case of protic solvents, and a multiparameter approach has been proposed to separate the effects of the solvent polarity, hydrogen bond donor ability and hydrogen bond acceptor ability on spectroscopic and kinetic properties [17, 18].

Finally, solvent effects on fluorescence spectra have recently been reviewed in depth [19] and are classified in terms of general and specific effects; the former are determined by the electronic polarizability (related to the solvent refractive index) and the molecular polarizability (related to the solvent dielectric constant) while the latter are attributed to hydrogen bonding, acid-base chemistry or charge transfer interactions as appropriate.

We adopt this approach in the present study, noting that while *N,N*-dimethyl-2-aminoanthracene (2-DMA) should not be susceptible to hydrogen bonding as a donor, and to an even lesser extent as an acceptor, the well-studied 2-aminoanthracene (2-AA) should be affected in both cases, and a comparative study should enable some discrimination between the various approaches outlined above.

2. Experimental details

All the organic solvents used were of the highest grade commercially available, while water was doubly distilled. 2-AA (Sigma) was recrystallized twice from benzene (melting point, 237 - 240 °C (literature value, 238 - 239 °C [20])). 2-DMA was synthesized by the thermolysis of 2-dimethyl-aminoanthracene methiodide under reduced pressure (180 °C, 0.1 mmHg). Recrystallization from acetone-water gave an 82% yield of bright yellow crystals (melting point, 155 °C (literature value, 155 °C [20])). 2-Dimethyl-aminoanthracene methiodide was synthesized by the methylation of 2-AA by methyl iodide according to a literature procedure [20] but with a yield of only 13.8% (melting point, 208 - 211 °C (literature value, 215 °C)). The structure of 2-DMA was confirmed spectroscopically; thus the mass spectrum showed base peaks 221 (100%), 205 (12.66%), 178 (27.67%), 165 (14.32%), 151 (3.15%); the proton magnetic resonance spectrum (solvent, $CDCl_3$) showed the following δ (ppm): 8.28 (1H, s, 10-H), 8.18 (1H, s, 9-H), 7.91 (4H, m), 7.35 (2H, m), 6.99 (1H, s, 3-H), 3.08 (6H, s, 2Me). Absorption spectra were measured using a Shimadzu 365 UV-visible-

IR recording spectrophotometer. Fluorescence spectra were recorded using a Perkin-Elmer model MPF-3 spectrofluorometer. All optical measurements were carried out at 20 ± 1 °C. Proton magnetic resonance spectra were obtained using a Perkin-Elmer R-34 (220 MHz) instrument. Mass spectra were obtained using a Kratos Ltd. model MS80 instrument.

3. Results and discussion

Absorption and fluorescence data for 2-AA and 2-DMA in 19 solvents are collated in Table 1. There is no discernible effect (more than a few nanometres) of solvent polarity on the absorption maxima $\bar{\nu}_A$, whereas the emission maxima $\bar{\nu}_F$ and hence the Stokes shifts $\Delta\bar{\nu}_{SS}$ ($\Delta\bar{\nu}_{SS} = \bar{\nu}_A - \bar{\nu}_F$) are strongly solvent dependent, being positively correlated with solvent polarity. We have concentrated on two equations that are taken as being representative of the two different overall approaches discussed in Section 1. Firstly, the expression of Bilot and Kawski [22]

$$\Delta\bar{\nu}_{SS} = \frac{(\mu_e - \mu_g)^2}{hca^3} \left[\frac{(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 2)}{\{1 - \beta(n^2 - 1)/(2n^2 + 2)\}^2 \{1 - \beta(\epsilon - 1)/(2\epsilon + 2)\}} \right] + \text{constant} \quad (1)$$

$$= \frac{(\mu_e - \mu_g)^2 \text{BK}}{hca^3} + \text{constant} \quad (2)$$

correlates $\Delta\bar{\nu}_{SS}$ with polarizability functions through $(\mu_e - \mu_g)$, *i.e.* the difference between the dipole moments of the excited and ground states [6, 23 - 25]. The other terms are as follows: ϵ , solvent dielectric constant; n , solvent refractive index; β , a factor approximately equal to unity; a , the solute cavity radius, taken as 5.5 Å for both 2-AA [23] and 2-DMA; h and c are the normal universal constants. Values of the polarizability function, designated BK in eqn. (2), are listed in Table 1 while $\Delta\bar{\nu}_{SS}$ is plotted against BK in Fig. 1 and Fig. 2 for 2-AA and 2-DMA respectively.

From Fig. 1 it is clear that solvents 1 - 11 and 13 give an excellent correlation according to eqn. (1), and the regression line is given by eqn. (3).

$$\Delta\bar{\nu}_{SS} = (2898 \pm 148) + (1126 \pm 304)\text{BK} \quad (3)$$

where $\Delta\bar{\nu}_{SS}$ is in reciprocal centimetres. From eqn. (3), $(\mu_e - \mu_g)$ can be estimated as 6.1 D which is similar to the values given previously of 6.1 D [23] and 5.4 D [26]. The solvents which deviate strongly and positively from the regression line in Fig. 1 are all hydroxylic solvents, while all those adhering to it are non-hydroxylic. If the deviation is due to the specific effect of hydrogen bonding in the *ground* state between proton-accepting 2-AA and proton-donor solvents [23] which is completely lost on excitation to $^1(2\text{-AA})^*$, which is highly acidic, then the deviation should be much

TABLE 1
Solvent effects on the Stokes shifts of 2-AA and 2-DMA

Solvent	Number	$E_T(30)^a$ (kJ mol^{-1})	BK ^b	2-AA		2-DMA			
				λ_A (nm)	λ_F (nm)	$\Delta\nu_{SS}$ (cm^{-1})	λ_A (nm)	λ_F (nm)	$\Delta\nu_{SS}$ (cm^{-1})
Cyclohexane	1	130.5	-0.001	396	437	2369	414	458	2320
Toluene	2	138.9	0.031	401	447	3056	420	478	2889
Benzene	3	144.2	0.008	402	457	2994	421	481	2962
Dioxan	4	150.6	0.043	406	471	3399	419	485	3248
Tetrahydrofuran	5	156.5	0.550	401	476	3929	419	493	3583
Chlorobenzene	6	156.9	0.399	402	458	3041	423	483	2937
Bromobenzene	7	156.9	0.361	403	459	3027	424	487	3051
Chloroform	8	163.6	0.372	398	461	3434	420	496	3648
Pyridine	9	168.2	0.639	416	496	3877	425	502	3609
Dichloromethane	10	172.0	0.586	400	462	3355	421	492	3427
Acetone	11	176.6	0.793	409	483	3746	419	500	3866
2-Methyl-2-propanol	12	183.7	0.673	403	496	4652	412	485	3653
Acetonitrile	13	192.5	0.864	410	485	3772	419	505	4065
2-Butanol	14	197.1	0.734	404	495	4550	414	487	3621
2-Propanol	15	203.3	0.766	403	493	4530	414	489	3705
1-Butanol	16	210.0	0.754	404	492	4427	416	488	3547
Ethanol	17	217.2	0.812	403	490	4405	415	490	3688
Methanol	18	232.2	0.858	401	493	4654	415	494	3854
Ethanediol	19	236.8	—	403	496	4652	420	506	4047

^a From ref. 14.

^b Calculated from data in ref. 21 according to the Bilot-Kawski equation (see text); values of ϵ and n refer to 20 °C.

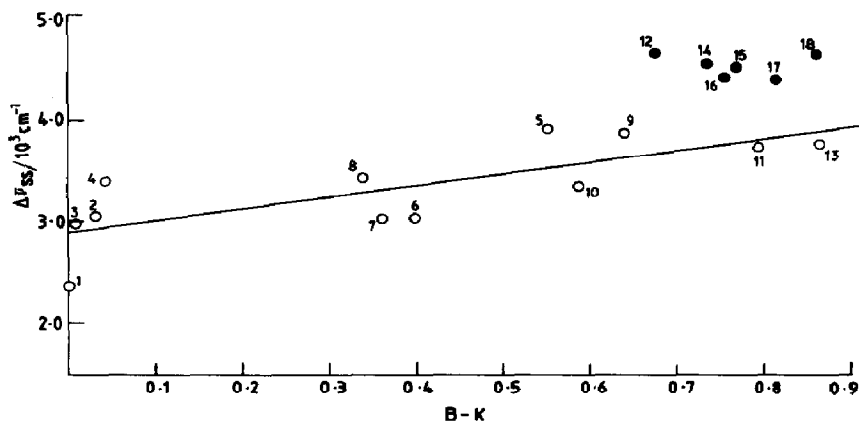


Fig. 1. Correlation of the Stokes shift $\Delta\bar{\nu}_{SS}$ of 2-AA with the value of BK (see eqn. (1)). Full circles refer to alcoholic solvents (which are excluded from the regression analysis).

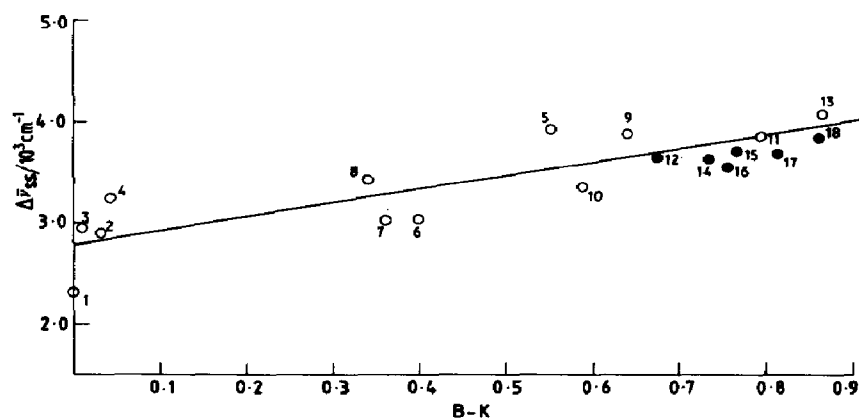


Fig. 2. Correlation of the Stokes shift $\Delta\bar{\nu}_{SS}$ of 2-DMA with the value of BK (see eqn. (1)). Full circles refer to alcoholic solvents (which are excluded from the regression analysis).

reduced for 2-DMA by virtue of the steric inhibition of its acceptor function. Figure 2 indicates that an excellent correlation is achieved for the non-hydroxylic solvents for 2-DMA, according to

$$\Delta\bar{\nu}_{SS} = (2786 \pm 132) + (1330 \pm 271)BK \quad (4)$$

where $\Delta\bar{\nu}_{SS}$ is in reciprocal centimetres, while the hydroxylic solvents show a consistent small negative deviation from this equation. From eqn. (4), a value for $(\mu_e - \mu_g)$ of 6.63 D is obtained for 2-DMA, consonant with the expected development of additional positive charge at the *N*-atom on excitation relative to 2-AA. A very recent study reports strong positive deviation for 1-butanol and water from plots of the Bakhshiev equation for both 1-aminonaphthalene and *N,N*-dimethyl-1-aminonaphthalene for values of the polarizability function exceeding 1.0 [27].

The second analysis correlates $\Delta\bar{\nu}_{SS}$ with the Dimroth parameter $E_T(30)$, as given in Fig. 3 and Fig. 4 for 2-AA and 2-DMA respectively. Since $E_T(30)$ includes contributions from hydrogen bonding, the good

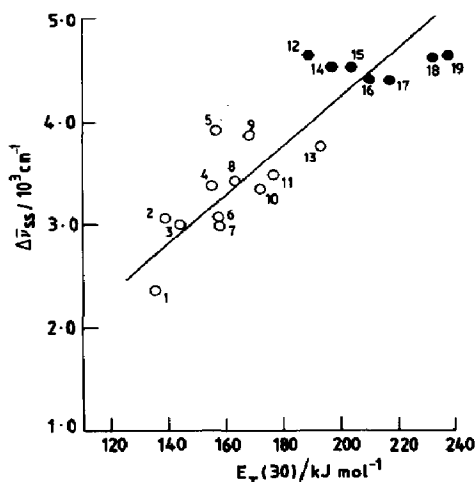


Fig. 3. Correlation of the Stokes shift $\Delta\bar{\nu}_{SS}$ of 2-AA with the Dimroth solvent polarity parameter $E_T(30)$.

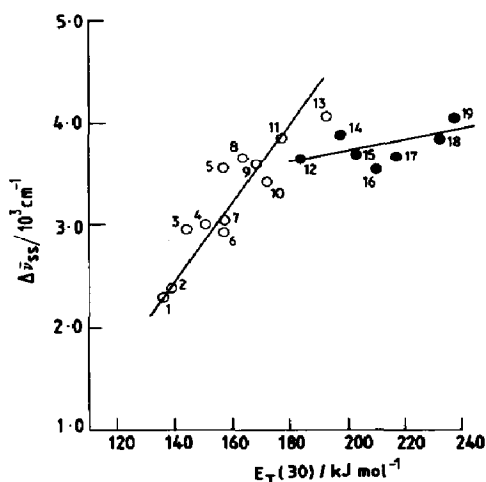


Fig. 4. Correlation of the Stokes shift $\Delta\bar{\nu}_{SS}$ of 2-DMA with the Dimroth solvent polarity parameter $E_T(30)$.

correlation found for 2-AA is not unexpected, while the absence of these contributions in the case of 2-DMA results in the separate correlations found for hydroxylic and non-hydroxylic solvents in Fig. 4. (All the data for 2-AA and those for 2-DMA in *non-hydroxylic* solvents lie on a single line.) Such separate correlations with $E_T(30)$ are a feature of a recent study [28] and have also been observed previously [11].

TABLE 2

Effect of solvent polarity (dioxan-water mixture) on $\bar{\nu}_F$ of 2-AA and 2-DMA

Solvent	[dioxan]:[water] (vol.%)	$E_T(30)$ solvent polarity parameter ^a ($\times 10^3$ cm ⁻¹)	$\bar{\nu}_F$ ($\times 10^2$ cm ⁻¹)	
			2-AA	2-DMA
1	100:0	12.59	212.31 (471) ^b	206.18 (485)
2	98:2	14.48	210.08 (476)	204.91 (488)
3	96:4	15.00	209.20 (478)	203.25 (492)
4	94:6	15.56	207.46 (482)	202.83 (493)
5	90:10	16.33	206.61 (484)	202.42 (494)
6	85:15	16.79	205.76 (486)	201.20 (497)
7	80:20	17.14	204.91 (488)	200.40 (499)
8	70:30	17.80	204.29 (489)	199.60 (501)
9	60:40	18.29	203.66 (491)	198.41 (504)
10	50:50	18.74	203.25 (492)	197.62 (506)
11	40:60	19.44	202.83 (493)	197.23 (507)
12	30:70	20.00	202.42 (494)	196.85 (508)
13	20:80	20.49	202.02 (495)	196.85 (508)

^aFrom ref. 29.

^bThe values in parentheses are the corresponding wavelengths in nanometres.

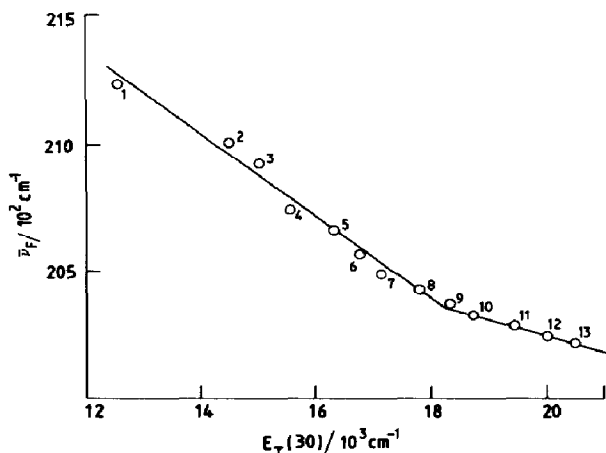


Fig. 5. Correlation of the fluorescence energy $\bar{\nu}_F$ of 2-AA with $E_T(30)$ for dioxan-water mixtures.

Dioxan-water mixtures afford a wide range of values of $E_T(30)$ while restricting other solvent-variable parameters to those of just two solvents, and have attracted interest as a probe for specific effects on fluorescence [29, 30]. A short investigation of the dependence of the fluorescence maximum $\bar{\nu}_F$ upon solvent composition was carried out both for 2-AA and 2-DMA and the results are presented in Table 2 and Figs. 5 and 6. In this case, remarkably parallel behaviour is shown by the molecules since $\bar{\nu}_F$ decreases linearly with increasing $E_T(30)$ until an inflection is reached at 40% water (2-AA) or 50% water (2-DMA), after which the further red shift with increasing $E_T(30)$ is halved. This type of effect has been reported [11, 29, 30] before and is attributable to increasing solvation of the S_1 state by water molecules which impart an enhanced solvent-structuring effect [11], although in one case a change in geometry of the emitting species was proposed [30]; this effect would be expected to be rather small for aminoanthracenes, although a recent study on aminonaphthalenes suggests otherwise [27].

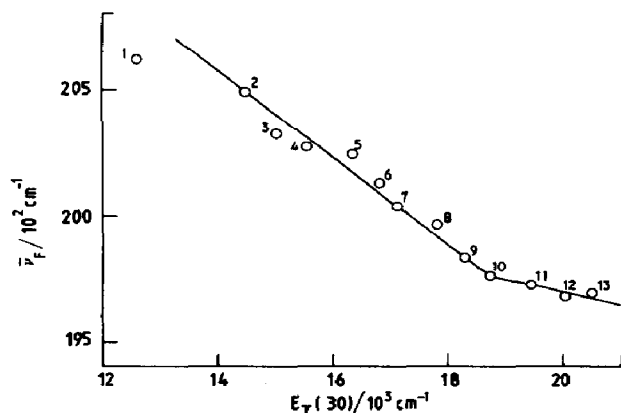


Fig. 6. Correlation of the fluorescence energy $\bar{\nu}_F$ of 2-DMA with $E_T(30)$ for dioxan-water mixtures.

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