Solvent Effects on Electronic Transitions of Highly Dipolar Dyes: A Comparison of Three Approaches

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The solvatochromism of several polar solutes, including some that contain both hydrogen bond-donating and -accepting properties (coumarins 1, 102, 120, 151, 152, and 153; nile red; and 4-aminofluorenone), is analyzed in terms of three models: the Reichardt single parameter E_T^N polarity scale, the multiparameter Kamlet−Taft equation, and the reaction field model. We use a "step-forward" procedure to determine which terms of the Kamlet−Taft equation are statistically significant in fitting the data. These equations provide the best fits to the data in almost all cases. We also find a correlation between the parameters *s* and *a*, which quantify the effects on the transition energy related to the solvatochromic parameters π^* and α, respectively. This relationship suggests that the magnitude of *a* is not indicative of the strength of the hydrogen-bonding interaction, but rather reflects the additional field produced from the dipole moment of a hydrogen bond-donating molecule that is held in an orientation that roughly parallels the solute dipole.

Introduction

Solvent effects on solute structure, reactivity, and properties are important aspects of solution chemistry. One key approach to understanding solvent effects is solvatochromism, the solvent-induced changes in the electronic transitions of solutes.[1−5] Theoretical and experimental investigations of these effects, in a variety of contexts, continue to be active areas of research.[6−11]

Numerous methods for describing solvatochromism in terms of solvent characteristics have been proposed. One simple approach has been to characterize these effects in terms of an empirical solvent polarity scale.[12] In many cases the scale is based on spectral data from a single solute molecule, or by averaging the results from a few solutes. One such scale, $E_T(30)$, is based on a negatively solvatochromic pyridinium *N*-phenolate betaine dye. Values of $E_T(30)$ (and its normalized version, E_T^N) have been determined for a wide variety of solvents,[2] making it a common choice for characterizing the overall solvation effect with a single parameter. For example, this parameter has been used recently to investigate the "polarity" of room-temperature ionic liquids.[6,13] The implicit assumption of this approach is that the transition energy of a given probe in a variety of solvents will display a linear dependence on this single parameter, resulting in a relationship such as

$$\nu = \nu_0 + qE_T^N \qquad (1)$$

where ν_0 is the transition energy of the probe in the absence of any solvent effect (gas phase) and *q* is a constant characterizing the solute. As has been pointed out previously,[2] this assumption is only likely to be appropriate when the solute−solvent interactions found with the probe under investigation are similar to those encountered by the reference dye.

Because a wide variety of solvent−solute interactions, both specific and nonspecific, may be responsible for the solvent effect on the properties of a given solute, a multiparameter equation that independently quantifies these various influences can be useful. The empirical solvatochromic comparison method developed and refined by Taft, Kamlet, and co-workers,[14−23] in which the various aspects of solvent effects on the spectra of numerous solutes are parametrized in a multiterm solvatochromic equation, has been widely used for the past three decades. For solvents that are neither aromatic nor halogenated, the general form of the Kamlet−Taft solvatochromic equation describing the transition energy is

$$\upsilon = \upsilon_0 + a\alpha + b\beta + s\pi^* \qquad (2)$$

where α and β measure the hydrogen bond donating and accepting ability of the solvent, and π^* its polarity/polarizability.[14−16] In this equation, *a*, *b*, and *s* are constants characteristic of the solute, and their magnitudes (and sign) reflect the relative influence of the corresponding solvent−solute interactions on the electronic transition energy.

In contrast, the reaction field approach[24−27] is based on a dielectric continuum model and contains (in principle) no adjustable parameters. The magnitude and direction of the shift in transition energy from that in the gas phase are determined by the dielectric constant (ϵ_0) and index of refraction (*n*) of the solvent, and by the ground and excited-state dipole moments (μ_i) of the solute and the radius (*a*) of the (assumed spherical) solvent cavity. The specific relationship is presented in eq 3:

$$\upsilon_{1-2} = \upsilon_0 + A_U[F(\epsilon_0,n)] + B_U\left[\frac{n^2-1}{n^2+2}\right] \qquad (3)$$

where A_U and B_U are given by

$$A_U = \frac{2\mu_1(\mu_1-\mu_2)}{hca^3} \qquad B_U = \frac{{\mu_1}^2-{\mu_2}^2}{hca^3} \qquad (4)$$

and

$$F(\epsilon_0,n) = \frac{\epsilon_0-1}{\epsilon_0+2} - \frac{n^2-1}{n^2+2} \qquad (5)$$

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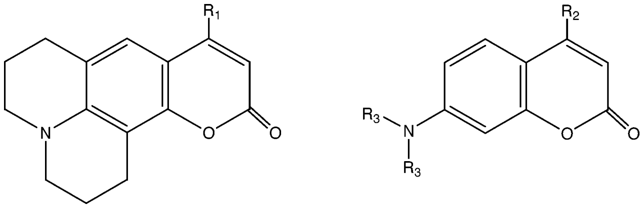

Figure 1. Structures of various coumarins: coumarin 1 (C1), $R_2 = CH_3$, $R_3 = C_2H_5$; coumarin 102 (C102), $R_1 = CH_3$; coumarin 120 (C120), $R_2 = CH_3$, $R_3 = H$; coumarin 151 (C151), $R_2 = CF_3$, $R_3 = H$; coumarin 152 (C152), $R_2 = CF_3$, $R_3 = CH_3$; coumarin 153 (C153), $R_1 = CF_3$.

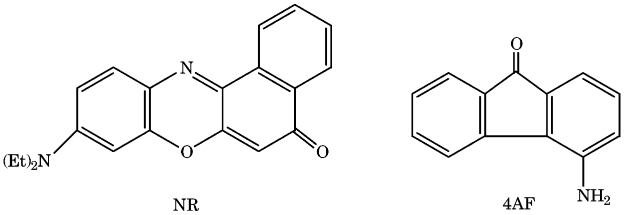

Figure 2. Structures of nile red (NR) and 4-aminofluorenone (4AF).

Although the Onsager functions $F(x) = 2(x - 1)/(2x + 1)$ are more widely used in the formulation of the reaction field expression,[1] we employ the Debye polarity functions for consistency with prior reports.[27,28] In any case, it has been pointed out previously that the two formulations "are in effect so close as to be virtually indistinguishable in solvatochromic shift measurements."[3]

Recently,[28] we showed that the Kamlet−Taft solvatochromic comparison method, eq 2, generally provides a better description of the solvent effects on the absorption and emission spectra of several coumarin dyes than does the reaction field model. We observed a greater difference in the quality of the fits of the two models as the hydrogen bond-accepting ability of the coumarin increases, not a surprising result given that the reaction field model does not account for any specific solvent−solute interactions. In this paper, we extend this investigation to a broader range of solutes, including some that contain both hydrogen bond-donating and hydrogen bond-accepting groups. We also introduce a stepwise multivariable regression analysis to determine which of the Kamlet−Taft solvatochromic parameters are significant in fitting the data for each system. We examine the solute parameters obtained by this analysis, and provide an interpretation of their significance.

Experimental Methods

Laser-grade solutes were obtained from Aldrich, Acros Organics, or Eastman Chemical and used as received. The structures of all eight probes are shown in Figures1 and 2. Solvents were obtained from Aldrich and were spectroscopic or anhydrous grade if available. Otherwise, the highest purity grade was used. The alkanes (with the exception of Decalin) were distilled over calcium hydride in a nitrogen atmosphere prior to use, and then stored over 3A molecular sieves. All other solvents were used as received and then stored over 3A or 4A sieves. The solvents are listed in Table 1, along with relevant physical parameters and solvatochromic values.

All spectra were recorded at 297 K. Absorption spectra were collected with a Perkin-Elmer Lambda 6, Perkin-Elmer Lambda 40, or a Hitachi U-3000 spectrophotometer. Fluorescence spectra were obtained on samples with maximum absorbance of less than 0.1 in a 1-cm cuvette with a SPEX Fluorolog 111. Following background subtraction, fluorescence spectra were corrected for instrument response.[29] The transition energy, ν, was generally calculated by using eq 6:

TABLE 1: Solvent Properties[a]

solvent	π^*	α	β	E_T^N	ϵ_o	n	$F(\epsilon_o,n)$
hexane	−0.11	0	0	0.009	1.88	1.370	0.00
heptane	−0.06	0	0	0.012	1.92	1.385	0.00
methylcyclohexane	0.00	0	0	0.006	2.02	1.424	0.00
decalin	0.09	0	0	0.015	2.15	1.480	−0.01
butyl ether	0.18	0	0.46	0.071	3.08	1.397	0.17
diethyl ether	0.24	0	0.47	0.117	4.20	1.350	0.30
ethyl acetate	0.45	0	0.45	0.228	6.02	1.370	0.40
tetrahydrofuran	0.55	0	0.55	0.207	7.58	1.405	0.44
propylene carbonate	0.83	0	0.40	0.472	64.92	1.420	0.70
dimethylformamide	0.88	0	0.69	0.386	36.71	1.428	0.67
dimethyl sulfoxide	1.00	0	0.76	0.444	46.45	1.478	0.66
acetone	0.62	0.08	0.48	0.355	20.56	1.356	0.65
acetonitrile	0.66	0.19	0.31	0.460	35.94	1.342	0.71
2-methyl-2-propanol	0.41	0.68	1.00	0.389	12.47	1.390	0.56
2-propanol	0.48	0.76	0.95	0.546	19.92	1.375	0.63
1-butanol	0.47	0.79	0.88	0.586	17.51	1.397	0.61
ethanol	0.54	0.83	0.77	0.654	24.55	1.359	0.67
methanol	0.60	0.93	0.62	0.762	32.66	1.327	0.71

[a] ϵ_o and n values are predominantly from the listing in ref 27. The values for those solvents not listed in that paper are from the following: Weissgerber, A. *Organic Solvents*, 2nd ed.; Wiley Interscience: New York, 1970. All values are for 25 °C except for heptane, methylcyclohexane, butyl ether, and butyl acetate which are at 20 °C. $F(\epsilon_o,n)$ is as defined in eq 5. E_T^N values are from ref 2 except for methylcyclohexane (estimated based on a value of 0.006 for cyclohexane). Values for α and β are from ref 22, as are π^* values for the alcohols. For all other solvents, π^* values are from ref 23 except for methylcyclohexane (estimated based on the value of 0 for cyclohexane).

$$\nu = \frac{\lambda_h^{-1} + \lambda_l^{-1}}{2} \qquad (6)$$

where λ_h and λ_l are the wavelengths corresponding to the points, on the high- and low-energy sides, respectively, at which the spectrum exhibits half of its maximum intensity. (The few exceptions are noted in Table 2.) This simple expression, which provides a reproducible and readily obtainable energy for each spectrum, has been used previously in similar contexts.[28,30] All reported energy values are the average of between two and five separate measurements.

Some of the data presented here for C1, C102, C152, and C153 have been reported previously.[28] We have repeated many of these measurements under conditions in which water has been more stringently excluded; thus, in those cases where discrepancies arise, the more recent results should be considered to replace those reported previously. In addition, the values of π^* used here for the alcohols are different than those in our previous work, with those reported here being more commonly used for the investigation of spectroscopic correlations. These changes have relatively little impact on the quality of the fits to the data. The most significant difference is a general decrease of 10−25% in the values of a for the fits to the solvatochromic model, compared to those determined previously.[28]

There are two statistical analyses relevant to our model-testing procedures. To describe our approach we introduce several terms related to the analysis of variance (ANOVA). We define

$$SS(\text{fit}) = \sum_i (y_i^{\text{obs}} - y_i^{\text{fit}})^2 \qquad (7)$$

TABLE 2: Absorption and Emission Energies, ν^a

solvent	C1 abs	C1 em	C152 abs	C152 em	C102 abs	C102 em	C153 abs	C153 em	C151 abs	C151 em	C120 abs	C120 em	NR abs	NR em	4AF abs	4AF em
hexane	28.67	25.57	27.24	23.59	27.77	24.60	25.67	22.23	29.24	24.81	30.72	26.54	20.69	18.24	24.08	19.62
heptane	28.66	25.53	27.10	23.54	27.67	24.71	25.55	22.22	29.18	24.78	30.61	26.59	20.60	18.21	24.01	19.56
MCH	28.54	25.46	26.98	23.44	27.66	24.60	25.49	22.13	29.06	24.70	30.57	26.48	20.48	18.13	23.95	19.50
decalin	28.37	25.32	26.81	23.28	27.52	24.32	25.16	21.99	28.86	24.49	30.43	26.24	20.31	17.96	23.83	19.42
butyl ether	28.32	24.77	26.63	22.17	27.46	23.96	25.14	21.05	27.80	22.80	29.82	25.31	20.12	17.42	23.15	18.04
diethyl ether	28.37	24.56	26.48	21.67	27.41	23.62	24.95	20.82	27.68	22.62	29.73	25.28	20.01	17.16	22.94	17.95
ethyl acetate	28.08	23.92	26.16	20.58	27.09	22.97	24.67	19.74	27.59	21.94	29.69	24.85	19.60	16.61	22.75	17.33
THF	27.86	23.88	26.04	20.58	26.97	23.00	24.45	19.72	27.17	21.82	29.28	24.79	19.40	16.53	22.43	16.81
PC	27.37	22.76	25.52	19.43	26.60	21.78	23.95	18.76	27.24	20.99	29.28	24.05	18.85	15.87	22.38	16.27
DMF	27.36	22.86	25.45	19.36	26.38	21.86	23.92	18.74	26.52	20.63	28.70	23.80	18.75	15.86	21.75	16.05
DMSO	27.07	22.55	25.23	18.99	26.21	21.66	23.72	18.39	26.25	20.31	28.45	23.47	18.52	15.66	21.38	15.59
acetone	27.68	23.22	25.86	19.85	26.72	22.26	24.45	19.12	27.28	21.31		24.38	19.16	16.14	22.37	16.73
acetonitrile	27.47	22.83	25.77	19.64	26.55	21.83	24.15	18.92	27.60	21.16	29.64	24.19	18.94	15.98	22.59	16.30
2-Me-2-PrOH	27.50	22.91	25.82	19.92	26.41	21.88	24.25	19.22	26.25	20.74	28.58	23.43	18.82	15.98	22.29	15.44
2-propanol	27.20	22.52	25.64	19.52	26.22	21.57	24.08	18.85	26.35	20.56	28.55	23.25	18.72	15.75	(22.20)	15.13
1-butanol	27.23	22.33	25.58	19.42	26.17	21.39	24.03	18.74	26.37	20.46	28.48	23.13	18.68	15.77	(22.20)	15.29
ethanol	27.27	22.19	25.62	19.28	26.16	21.16	24.03	18.56	26.58	20.41	28.58	23.11	18.63	15.62	(22.26)	14.90
methanol	27.09	21.90	25.64	18.98	26.05	20.97	23.99	18.33	26.80	20.24	28.79	22.99	18.50	15.48	(22.32)	14.60

[a] Transition energies, ν, are as described in eq 6 and are in units of 10^3 cm^{-1}. The uncertainty in each value is estimated to be 20 cm^{-1}. Those values in parentheses were not obtained with eq 6, but are estimates based on the observed absorption maximum.[32] Abbreviations: MCH, methylcyclohexane; THF, tetrahydrofuran; PC, propylene carbonate; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; 2-Me-2-PrOH, 2-methyl-2-propanol.

and

$$SS(\text{data}) = \sum_i (y_i^{\text{obs}} - \bar{y})^2 \tag{8}$$

where y_i^{obs} is the experimentally observed energy, y_i^{fit} is the energy calculated from a fit to the data, and $\bar{y}$ is the mean experimental energy of a given data set. The goodness-of-fit parameter R^2 can then be expressed as

$$R^2 \equiv 1 - \frac{SS(\text{fit})}{SS(\text{data})} \tag{9}$$

In essence, R^2 gives the percentage of the variation in the observed energies that is explained by the model. In general, the "best" model is the one that provides the largest percentage "explanation" of the data, suggesting that the model with the highest value of R^2 is most appropriate. However, because R^2 will necessarily increase as the number of fit parameters increases, an adjustment is necessary for comparisons made between models with different numbers of parameters. The standard approach for dealing with this situation is to use the adjusted R^2 (adj R^2), which statistically accounts for the number of independent variables in each model:

$$\text{adj } R^2 \equiv 1 - \frac{SS(\text{fit})/(N - p)}{SS(\text{data})/(p - 1)} \tag{10}$$

Here, N is the number of data points and p the number of fit parameters. To choose between the three models for a given data set, we select the one giving the highest value of adj R^2.

The F-statistic or F-ratio is defined by

$$F \equiv \frac{\{SS(\text{data}) - SS(\text{fit})\}/(p - 1)}{SS(\text{fit})/(N - p)} \tag{11}$$

F measures the reduction in the variance resulting from the fit and can be used to determine if the inclusion of an additional parameter in the equation leads to a statistically significant improvement in the fit. If F increases when a new variable is introduced, then the additional term is considered to significantly reduce *SS(*fit*)* and the term is retained; conversely, if F decreases, this indicates that the introduction of the new variable does not significantly reduce *SS(*fit*)* and the term is rejected. This is a well-known approach referred to as a "step-forward" procedure.[31]

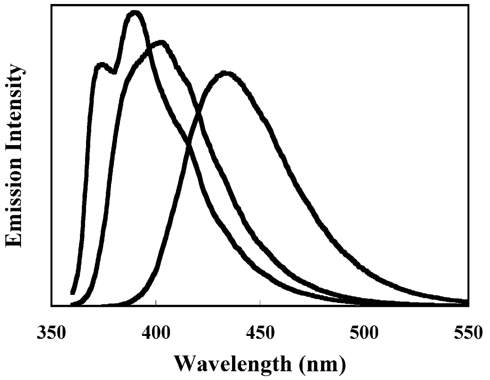

Figure 3. Emission spectra of C1 in methylcylcohexane (left), butyl ether (center), and acetonitrile (right). The emission intensity is arbitrary.

All statistical analyses were performed with Datadesk 6.1 software.

Results

Figure 3 shows a typical example of the solvent effect on the lowest energy peak of the electronic spectrum of these probes. In highly polar solvents, this peak is generally featureless. In the alkanes and less polar solvents, some broad shoulders appear, and in some cases two distinct peaks (or additional features) are present. Although more sophisticated analyses (for example, curve-fitting to a log-normal function) are possible, the average frequency defined by eq 6 provides a simple way to quantify the transition energies independent of substantial changes in line shape. This approach is also consistent with the analysis presented in our previous report.[28]

With the exception of the absorption spectrum of 4AF, this lowest energy feature is clearly separated from any other spectral peak, so that eq 6 can be easily applied. For the absorption spectra of 4AF in four of the alcohols, eq 6 cannot be used because of the presence of a second, stronger absorption at slightly higher energy. For these cases, we estimated the value

TABLE 3: Representative Fitting Results from Eq 2[a]

	ν_0	s	a	b	F
C120 abs	30.25 (0.41)	−1.99 (0.78)			26
	30.42 (0.25)	−1.75 (0.46)	−1.13 (0.40)		55
	30.63 (0.13)	−0.77 (0.29)		−1.84 (0.28)	250
	30.61 (0.09)	**−0.95 (0.21)**	**−0.40 (0.18)**	**−1.43 (0.26)**	**386**
C102 em	24.15 (0.59)	−3.4 (1.1)			38
	24.45 (0.13)	**−3.02 (0.24)**	**−1.95 (0.21)**		**587**
	24.55 (0.50)	−2.2 (1.1)		−1.9 (1.1)	40
	24.44 (0.14)	−3.07 (0.34)	−2.00 (0.31)	+0.10 (0.44)	371
C152 abs	26.88 (0.17)	−1.84 (0.32)			131
	26.97 (0.07)	−1.73 (0.12)	−0.54 (0.11)		503
	27.03 (0.11)	−1.39 (0.23)		−0.69 (0.23)	232
	27.01 (0.05)	**−1.57 (0.13)**	**−0.39 (0.12)**	**−0.30 (0.16)**	**613**

[a] All values for the fit parameters (ν_0, s, a, b) are as defined in eq 2 and are in units of 10^3 cm^{-1}. The values in parentheses represent the 95% confidence limits. The four entries for each set of data represent four separate fits. In each case, the parameters from eq 2 that were included in the fit have a result presented in the table. The fit with the highest value of F (shown in bold) includes those parameters that are significant in describing the data.

of ν from the absorption maximum.[32] The absorption and emission energies for all eight of the solutes in the eighteen solvents are shown in Table 2. The aprotic solvents are listed first, followed by the five alcohols studied. Both solvent sets are arranged roughly in order of increasing “polarity” as measured by, for example, their values of $E_{\mathrm{T}}^{\mathrm{N}}$ or π^* (see Table 1). In general, there is a decrease in transition energy with increasing solvent polarity, as expected for transitions in which the excited state dipole moment is considerably larger than the ground-state dipole moment.[33] There is clearly a difference, however, in the magnitude of the solvent effect on these dyes, with the range of observed energies of a particular dye varying from as little as about 2000 cm^{-1} for some of the absorption energies to as large as 5000 cm^{-1} in the case of 4AF emission. There are also specific differences in the details of how the transition energies vary as a function of solvent. These differences are particularly evident in the results for the alcohols, the bottom five entries in the table. As mentioned above, these alcohols are listed in order of increasing “polarity"; they are also in order of increasing α and decreasing β. Note that for most of the cases, the transition energy shows a general decrease (with varying magnitude) toward the bottom of the column. However, this pattern is not observed for the absorption transitions of C151, C120, and 4AF. The unusual trend is most apparent for C151, for which there is a monotonic *increase* in energy. These variations in the general trends for different solutes are indicative of differences in the details of the solvent effects on the electronic transitions in these dyes.

Previously,[28] we showed that the solvatochromic model provides a better fit than the reaction field model for several of the dyes studied here. In that work, the solutes were all coumarins containing no hydrogen bond-donating groups; all data were fit to eq 2 omitting the β term (i.e., b was set equal to 0). Here, we make no assumptions concerning the presence or absence of the α or β terms in the solvatochromic equations for any given dye. We use a statistical analysis to determine which of these terms are significant in describing each data set. This analysis is not necessary for our other two models: eq 1 contains only one term (other than the constant term), and all terms in eq 3 are required by its theoretical construction. As described above, we use the “step-forward” fitting procedure to determine which terms in eq 2 are statistically significant in fitting the data. Table 3 shows the results of this procedure for three representative cases. For the C120 absorption data, the F-statistic is very low when only the π^* term is included in fits to eq 2. The addition of either the α term or the β term alone results in an increase in F, with the β term providing the larger increase. When all three terms are included, F is the largest of all, indicating that all three terms are significant in describing the dependence of the transition energy on solvent parameters. This result is chemically reasonable: C120 contains both hydrogen bond-donating and -accepting sites, so a dependence on both α and β is not surprising.

For C102 emission, the fit to the single solvatochromic parameter π^* again has a very low F value. The addition of the α term results in a large increase in F. When both α and β are included in the fit, however, F decreases substantially compared to the value with α alone. This result indicates that the inclusion of the β term is not significant in fitting the data, consistent with the chemical structure of the solute. There are no hydrogen bond-donating sites on C102, so there is no expectation that the electronic transition energy should depend on the hydrogen bond-accepting ability of the solvent.

Table 4 shows the results of this procedure for all 16 sets of transition energies. The significant solvatochromic parameters from eq 2 are presented, along with the corresponding values of F and adj R^2. The values of adj R^2 are all above 0.971, with 12 of the 16 fits having values of adj R^2 greater than 0.980. The average value is 0.986. Thus, all of the sets of data are well fit by eq 2 including π^* and one or both of α and β. In all but one instance, the resulting equations contain solvatochromic terms that are reasonable given the chemical structure of the solute species. The lone exception is for the absorption data for C152. In this case, the “step-forward” procedure results in an equation that includes a β term, even though there is no hydrogen bond-donating moiety in C152. Table 3 shows the details of the “step-forward” analysis for this case. The fit including β does have the highest value of F. This is an unexpected (and nonphysical) result. We note, however, that the magnitude of the b parameter in this fit is quite small, indicating a relatively weak dependence, and the reported uncertainty is over 50% of its magnitude.[34] Other than this one slight anomaly, this procedure provides a statistically valid method for obtaining chemically reasonable expressions in all cases.

Table 4 also shows the results of fits of the absorption and emission data to the other two models: the linear dependence on the polarity parameter $E_{\mathrm{T}}^{\mathrm{N}}$ given in eq 1 and the reaction field model of eq 3. The criterion for determining which of the three models best fits a particular set of data is the value of adj R^2; the highest value of adj R^2 for each set of data is shown in bold in the table. As a typical example, we examine the results for C120. For both absorption and emission data, the solvatochromic model has the highest value of adj R^2 and therefore is considered to be the most appropriate model. To provide a sense of the relative quality of fits with different values of adj R^2, the residuals $\nu_{\mathrm{calc}} - \nu_{\mathrm{exp}}$ for absorption and emission energies in C120 for the three models are presented in Figure 4. Note that the solvatochromic model displays relatively small residuals, whereas the spread is noticeably larger for the reaction field model. In particular, note that the relatively large residuals for the alcohols with the reaction field model (shown as open squares) are not randomly distributed about 0 as they are for the solvatochromic model (shown as filled squares). As we noted in our previous work,[28] the reaction field model fails to account for the separation of the data at high polarity values into two groupings, with the alcohols giving transition energies that are generally lower than those from polar aprotics of roughly comparable polarity. The $E_{\mathrm{T}}^{\mathrm{N}}$ model also shows larger residuals.

TABLE 4: Best Fits to Various Models[a]

	solvatochromic model						E_T^N model			reaction field model			
	ν_0	s	a	b	F	adj R^2	ν_0	q	adj R^2	ν_0	A_U	B_U	adj R^2
C1 abs	28.58	−1.40	−0.77		421	**0.980**	28.50	−2.24	0.891	29.79	−1.81	−7.14	0.914
	(0.07)	(0.12)	(0.11)				(0.15)	(0.38)		(0.50)	(0.16)	(2.01)	
C1 em	25.35	−2.96	−1.90		757	**0.989**	25.24	−5.12	0.946	25.86	−4.40	−1.36	0.930
	(0.11)	(0.20)	(0.18)				(0.23)	(0.59)		(1.87)	(0.60)	(7.48)	
C152 abs	27.01	−1.57	−0.39	−0.30	613	**0.991**	26.81	−2.27	0.761	28.66	−2.27	−6.65	0.983
	(0.05)	(0.13)	(0.12)	(0.16)			(0.24)	(0.61)		(0.44)	(0.14)	(1.78)	
C152 em	23.13	−4.52	−1.81		284	0.971	22.80	−6.49	0.829	24.60	−6.12	−5.01	**0.979**
	(0.14)	(0.45)	(0.20)				(0.56)	(1.42)		(1.38)	(0.44)	(5.54)	
C102 abs	27.66	−1.37	−0.96		733	**0.989**	27.60	−2.42	0.923	28.41	−2.08	−2.80	0.872
	(0.05)	(0.10)	(0.09)				(0.13)	(0.34)		(1.20)	(0.39)	(4.83)	
C102 em	24.45	−3.02	−1.95		587	**0.986**	24.34	−5.24	0.944	24.95	−4.50	−1.31	0.930
	(0.13)	(0.24)	(0.21)				(0.24)	(0.62)		(1.81)	(0.61)	(7.63)	
C153 abs	25.42	−1.71	−0.60		538	**0.984**	25.28	−2.34	0.782	27.10	−2.28	−6.60	0.974
	(0.07)	(0.12)	(0.10)				(0.23)	(0.58)		(0.57)	(0.18)	(2.27)	
C153 em	21.89	−3.80	−1.57		327	0.975	21.62	−5.53	0.843	23.14	−5.17	−4.30	**0.977**
	(0.19)	(0.35)	(0.31)				(0.46)	(1.15)		(1.22)	(0.39)	(4.88)	
C151 abs	29.06	−1.13	−0.18	−2.22	2406	**0.998**	28.56	−3.55	0.666	30.69	−3.41	−7.41	0.786
	(0.05)	(0.11)	(0.10)	(0.14)			(0.48)	(1.20)		(2.65)	(0.85)	(10.63)	
C151 em	24.45	−3.31	−1.23	−1.61	249	**0.978**	23.94	−6.34	0.818	25.45	−5.88	−4.01	0.935
	(0.23)	(0.54)	(0.49)	(0.69)			(0.57)	(1.44)		(2.37)	(0.76)	(9.50)	
C120 abs	30.61	−0.95	−0.40	−1.43	386	**0.986**	30.30	−2.83	0.727	31.84	−2.65	−5.49	0.790
	(0.09)	(0.21)	(0.18)	(0.26)			(0.34)	(0.86)		(2.10)	(0.67)	(8.44)	
C120 em	26.36	−2.19	−1.55	−1.02	785	**0.993**	26.13	−4.97	0.895	26.93	−4.25	−2.21	0.860
	(0.10)	(0.23)	(0.21)	(0.29)			(0.33)	(0.82)		(2.63)	(0.84)	(10.52)	
NR abs	20.47	−1.95	−1.01		1316	**0.994**	20.34	−3.04	0.879	21.73	−2.78	−4.78	0.948
	(0.05)	(0.10)	(0.08)				(0.22)	(0.55)		(0.99)	(0.32)	(3.98)	
NR em	17.96	−2.51	−1.23		381	**0.978**	17.80	−3.85	0.868	18.71	−3.53	−2.47	0.968
	(0.12)	(0.22)	(0.20)				(0.29)	(0.73)		(0.99)	(0.32)	(3.95)	
4AF abs	23.94	−1.58		−1.09	842	**0.990**	23.54	−2.58	0.605	26.01	−2.75	−8.81	0.894
	(0.07)	(0.15)		(0.16)			(0.39)	(0.99)		(1.42)	(0.46)	(5.68)	
4AF em	19.35	−3.06	−2.22	−1.18	512	**0.989**	19.07	−6.76	0.903	19.33	−4.01	−2.60	0.932
	(0.16)	(0.39)	(0.35)	(0.49)			(0.42)	(1.07)		(0.40)	(2.16)	(1.86)	
mean						**0.986**			0.830				0.917

[a] Solvatochromic model represents the fits to eq 2 with the largest value of F. E_T^N model represents the fits to eq 1. Reaction field model represents the fits to eq 3. All values for the fit parameters are in units of 10^3 cm^{-1}. The values in parentheses represent the 95% confidence limits in these fit parameters. Values for adj R^2 and F are defined in eqs 10 and 11, respectively. For each set of three fits, the model with the highest value of adj R^2 is shown in bold.

Particularly noticeable is the poor fit for the alcohols, for which the residuals are not only relatively large, but vary greatly from positive to negative. This is again a reflection of the inability of this model to properly account for the additional effects of specific hydrogen-bonding interactions.

Discussion

We now assess the relative merits of the three models more generally. A first observation is that the fits to E_T^N are never the best, and they are never as good as the fits with eq 2. The highest value of adj R^2 seen is 0.946; the average of the 16 fits is 0.830. These poor correlations are not surprising for several reasons. First, although E_T^N is known to be sensitive to hydrogen bond donation, its response measures the particular mix of this effect relative to nonspecific solvation that is characteristic of betaine 30. That is, E_T^N is well described by a solvatochromic equation including π^* and α, for which $a/s = 1.3$ (and $b = 0$).[2,35,36] As has been shown above, for all of the probes in this study, there is a very good fit to eq 2, and these fits all have $a/s < 1$; a poor correlation with E_T^N is thus expected. In addition, several of the probes have the capability of forming solute-to-solvent hydrogen bonds through the amine hydrogens. This is evidenced by the nonzero values of b in fits to eq 1 for C120, C151, and 4AF. The betaine dyes used to generate the E_T^N scale lack this capability; thus it is expected that E_T^N will not provide an appropriate measure of the solvatochromic effect in these cases. Kamlet et al.[37] previously made a similar analysis in providing a simpler explanation for the solvatochromism of several dyes than that implied by a correlation with the $E_T(30)$ parameter.[38]

The reaction field model, with an average value of adj R^2 of 0.917, provides a better fit than E_T^N in 12 of the 16 cases, and for many of these it is a significantly better fit. However, this model does not generally provide a good fit to the experimental data, and it is rarely equal (or superior) to the solvatochromic model. The highest value of adj R^2 for fits to eq 6 is 0.983; even for this case, the solvatochromic model shows a higher adj R^2. There are, however, two instances in which the reaction field model provides the best fit: for the emission energies of C152 and C153. Both C152 and C153 contain the highly electron-withdrawing trifluoromethyl group, which is expected to decrease the hydrogen bond-accepting ability of the probe compared to that of the equivalent species containing a methyl group (C1, C102). In both cases, the adj R^2 values for the solvatochromic model are close (and in the case of C153 extremely close), but not quite as high as those for the reaction field model. These cases are also the two *lowest* values of adj R^2 of all of the 16 fits with the solvatochromic approach. For the absorption energies for these two dyes, the solvatochromic model provides a better fit, but only slightly so (0.991 vs 0.983; 0.984 vs 0.974). For no other set of data is the adj R^2 for the reaction field model above 0.980. We have previously noted that when the alcohols are removed from the analysis, the fit to the reaction field model increases substantially for several of these coumarins.[28] These observations suggest that an inability

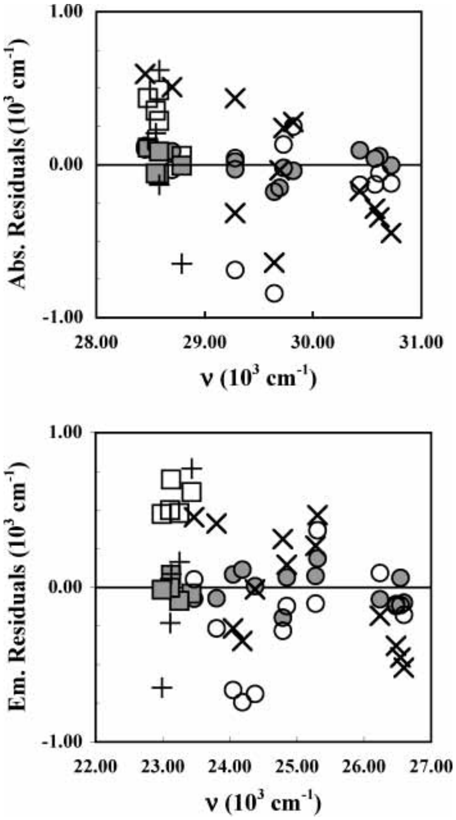

Figure 4. Residuals for C120, calculated as the difference between the energy predicted by the fit to one of the three models and the experimental energy for each of the three models, plotted against the experimental energy. The upper panel shows the absorption results and the lower panel shows the emission results. The solvatochromic model (eq 2) is represented by the filled symbols and the reaction field model (eq 5) is represented by the open symbols. For these two models, the circles represent aprotic solvents and the squares represent the alcohols. For the E_T^N model (eq 1), aprotic solvents are represented by × and alcohols are represented by +.

to account fully for hydrogen-bonding interactions prevents the reaction field model from generally providing the best fit, although it can be an adequate model in some circumstances, particularly when solvent−solute hydrogen bonding is expected to be relatively minimal.

We now turn our attention to an examination of the various solute fit parameters from the solvatochromic equation and any insight we can gain from them. In general, we will restrict our analysis to the results for the six coumarins because their structural similarities provide a simpler basis for drawing conclusions. We first examine the solute parameter *s*. For all of the solutes studied here, the magnitude of *s* is significantly greater for the emission energies than for the absorption energies, as shown in Table 4. In addition, in all cases, the permanent dipole moment is known to increase substantially upon electronic excitation.[30,39,40] Table 5 shows calculated dipole moments for the six coumarins.[41] These calculations reproduce experimentally determined values reasonably well[42] and are very similar to previously reported calculated values.[43] Figure 5 shows the correlation of $|s|$ with the dipole moment of the initial state of the electronic transition. A linear regression, shown by the solid line, gives $|s| = 0.38\mu - 0.74$; $R^2 = 0.93$. Because the π^* parameter measures a combination of polarity and polarizability of the solvent, it is perhaps not surprising that the complementary *s* parameter for the solute might be correlated with its dipole moment. To the extent that any solvent dipole/solute induced dipole interactions are roughly constant for all of the coumarins, the $s\pi^*$ term can then be thought of as predominantly describing the energy stabilization brought about by nonspecific dipole/dipole interactions. Previous authors[44] have noted this correlation of *s* for absorption energies with the ground-state dipole moment for two groups of solutes. To our knowledge this is the first demonstration of this simple relationship for both ground and excited-state dipole moments.

TABLE 5: AM1 Calculated Properties[41] of Various Coumarins[a]

	$\mu(S_0)$	$\mu(S_1)$	O charge (S_0)	O charge (S_1)	Δq
"C1"[b]	6.0	7.3	−0.317	−0.327	−0.010
C102	6.1	9.9	−0.332	−0.331	+0.001
C120	5.8	8.3	−0.316	−0.293	+0.023
C151	5.5	10.6	−0.272	−0.268	+0.004
C152	5.7	13.3	−0.273	−0.286	−0.013
C153	6.4	13.9	−0.298	−0.306	−0.008

[a] Dipole moments are in debyes. Charges are ESP fit charges for the carbonyl oxygen. Δq is the change in charge on the carbonyl oxygen ($S_1 - S_0$). [b] These values are for C311, an analogue of C1 in which the diethylamine group is replaced with a dimethylamine group.

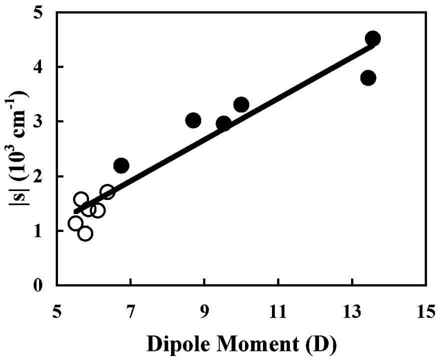

Figure 5. Correlation of $|s|$ from solvatochromic equation fits (eq 2) to ground- and excited-state dipole moments for the coumarins. Calculated dipole moments[41] are reported in Table 5 and *s* values are from Table 4. Open circles represent S_0 moments and absorption values; filled circles represent S_1 moments and emission values. The solid line is a least-squares fit to all of the data; $R^2 = 0.93$.

An examination of the *a* values is somewhat more complicated. For all eight dyes, the magnitude of the *a* term is always larger for emission than absorption, suggesting that hydrogen bond donation to the solute has a greater impact on emission than absorption energies. A recent molecular dynamics simulation demonstrates a clear hydrogen-bonding interaction at the carbonyl oxygen of C153 in methanol solution.[9] In addition, previous authors have suggested a linear relationship between $|a|$ and pK_a.[44] A relationship between $|a|$ and the negative charge at the carbonyl oxygen might thus be expected, based on the idea that the strength of the hydrogen-bonding interaction (and therefore the magnitude of the effect on the transition energy) would be enhanced by greater electron density. The calculated charge on the carbonyl oxygen for each of the coumarins is presented in Table 5.[41] A plot (not shown) of $|a|$ for absorption versus these charges in the ground state (S_0) shows a rough correlation ($R^2 = 0.68$). However, if the excited state (S_1) charges and emission values for $|a|$ are included in the analysis, there is essentially no correlation at all ($R^2 = 0.12$). Although there is a substantial increase in $|a|$ for all of the emission equations, there is relatively little corresponding change in the charge at the carbonyl oxygen. In addition, in three of the six cases there is actually a net *decrease* of negative charge at the carbonyl oxygen upon excitation. Previous investigations[39,43] have also reported relatively small changes in electron density at the carbonyl oxygen atom in coumarins. If the magnitude of

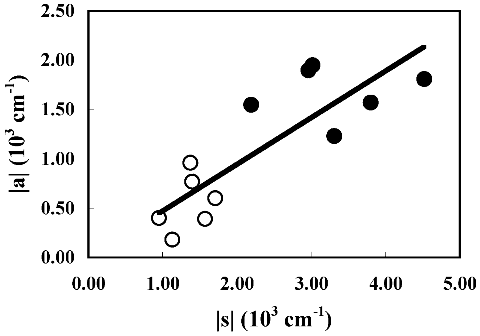

Figure 6. Correlation of $|a|$ with $|s|$ for the solvatochromic model, eq 2, as reported in Table 4. Open circles represent absorption parameters; filled circles represent emission parameters. The solid line represents a least-squares fit to all of the data; $R^2 = 0.68$.

a were related to the charge on the carbonyl oxygen, there would be essentially no change in a between the absorption and emission equations, and in some cases there would be a slight decrease. Instead, the magnitude of a increases substantially in each case. This increase is by roughly the same amount (950−1150 cm^{-1}) in all but one of the coumarins studied. (For C152, the change in a is about 1400 cm^{-1}.) Thus, the negative charge at the carbonyl oxygen cannot be used to explain the relative values of $|a|$ in these systems, particularly for the emission results.

In fact, $|a|$ seems to be more closely related to the dipole moment μ (although still very roughly) than to the negative charge on the oxygen atom. A regression of $|a|$ versus μ (plot not shown), including both absorption and emission results for the coumarins, results in $R^2 = 0.62$. Although this correlation is still not very strong, it is significantly better than the corresponding correlation ($R^2 = 0.12$) with the charge on the carbonyl oxygen. An even stronger relationship ($R^2 = 0.68$) is found between $|a|$ and $|s|$ for the coumarins, as shown in Figure 6. A possible explanation for this relationship involves a consideration of the nature of the hydrogen-bonding interaction at the carbonyl oxygen. We suggest that the α parameter provides a measure of the relative extent to which hydrogen bond donation to the solute occurs, holding one (or perhaps a few) solvent molecule in a particular, favorable, position. As mentioned above, molecular dynamics simulations show the presence of a hydrogen bond from methanol to this site in C153. Little change in this interaction is observed upon excitation from S_0 to S_1,[9] consistent with the lack of substantial change in the electron density at the carbonyl oxygen upon excitation. Assuming that all of the other coumarins in this study provide at least roughly equivalent (if not significantly better) hydrogen bond-accepting sites at the carbonyl oxygen, we expect that a specific solvent molecule maintains a relatively strong hydrogen bond to the coumarins in both the ground and excited states for all of the alcohols studied. The geometry of the complex, while not fixed, will have a distribution such that the alcohol dipole will tend to be roughly parallel to that of the solute.[9] Then, to the extent that this hydrogen bond is maintained, the alcohol's dipole moment will produce a significant nonzero electric field along the solute dipole direction. It is this persistent field that we propose contributes substantially to the α dependence of the solvatochromic equation. Thus, the a parameter for a given coumarin is correlated with the general polarity parameter (s) because the particular hydrogen-bonded solvent molecule merely provides an additional reaction field component similar to the nonspecific reaction field produced by an aprotic solvent. We interpret much of the additional spectral shifts found in the alcohols (and quantified by the α term in the solvatochromic equation) as not due to any important changes in the hydrogen bonding between the S_0 and S_1 states, but rather as just due to their sensitivity (as parametrized by $|s|$) to solvent-produced electric fields.

We next turn to an examination of the $b\beta$ term. First, we point out that the "step-forward" procedure results in $b = 0$ in 9 of the 10 cases for which we would chemically expect no dependence on the solvent hydrogen bond accepting ability. For the six equations that include $b\beta$ terms (excluding the nonphysical case described previously with C152) the three solutes (C120, C151, 4AF) all have amino groups that are capable of donating hydrogen bonds to the solvent. Recent experimental and theoretical investigations have shown the presence of hydrogen-bonding interactions at both the carbonyl oxygen and the amine functionality for gas-phase C151 complexes (and small clusters) with water and with methanol.[45−51] In general, there is a preference for hydrogen bond donation from the amine hydrogens over interactions at the carbonyl oxygen when there are small numbers of solvent molecules included in the model. Although calculations[39,41,43] show a decrease in electron density at the amine nitrogen upon excitation, there is very little change in the partial positive charge on the amine hydrogens, and excitation to S_1 does not appear to produce any large change in the hydrogen-bonding interaction at this site. This result is reminiscent of the situation at the carbonyl oxygen, for which there is also little change in charge, or hydrogen-bonding interaction, upon excitation from S_0 to S_1. However, unlike the situation described above for the a parameter, we do not observe a correlation of $|b|$ with $|s|$ or μ, as we might expect if the two situations were analogous. For the two coumarins, the emission equation appears to have a slightly lower magnitude of b than the absorption equation, although given the size of the uncertainties there may not be truly significant differences; for 4AF, the two are essentially unchanged. An explanation for this relative insensitivity of b to the electronic state of the solute is not readily apparent. More detailed analysis of modeling results examining the hydrogen-bonding interactions with the NH_2 group may provide further insight into this issue.

Conclusion

We have demonstrated that a "step-forward" statistical procedure can be used to determine the significant terms in the multiparameter solvatochromic equation description of electronic transition energies for a variety of dipolar solutes. These equations all provide very good fits, which are superior to the theoretically based reaction field approach in almost all cases. We also note a correlation between the solute parameters s and a, which quantify the effects on the transition energy related to the solvatochromic parameters π^* and α, respectively. Our interpretation of this relationship is that the magnitude of a is not related to the strength of the hydrogen-bonding interaction, but rather reflects the additional field produced when the dipole moment of a protic solvent molecule is held by a hydrogen bond in an orientation that roughly parallels the solute dipole.

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