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Characterization of solvatochromic probes: simulation of merocyanine 540 absorption spectra in binary solvent mixtures and pure solvent systems

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ABSTRACT: An empirical extension of the continuum model was used to reproduce the absorption spectrum of the optical probe merocyanine 540 in numerous solvents based on 27 probe-specific parameters in conjunction with the dielectric constant and refractive index of the solvent. The calibrated absorption spectrum of this dye allowed the accurate determination of the dielectric constant and refractive index of the bulk solvent. This study incorporates several binary solvent mixtures in addition to several pure solvents of differing functionality, including protic and aprotic solvents. A single, generally applicable, set of probe-specific parameters is presented. The accuracy of the determined solvent properties using this general set of probe parameters suggests that the influence of specific solvent–solute interactions on the absorption spectrum of this dye must be constant if not insignificant in the range of solvents studied, with the notable exception of water. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: merocyanine 540; cyanine dyes; continuum model; dielectric constant; refractive index

INTRODUCTION

It has long been recognized that solvatochromic shifts for suitable dyes could be used as a measure of a solvent's ability to stabilize the formation of ionic intermediates.[1–3] It has become a widespread practice to use empirical solvent polarity scales[4–7] to predict the influence of solvent on the position of chemical equilibria or on reaction rates. In common with all empirical relationships, these solvent polarity scales do not attempt to understand the nature of the interactions responsible for the solvatochromic effect. Instead, these relationships simply assume that the interactions that influence the spectral changes are similar in nature to those that influence the chemical phenomenon of interest. Extensions of these studies have explored non-ideal solution behavior,[8,9] microheterogeneous environments[10,11] and solvent structure near liquid interfaces.[12–14]

The main drawback of these relationships is the requirement for a predetermined empirical constant for the environment of interest against which the susceptibility of the probe of interest is to be tested. For example, the ET_{30}, Z or π^* numbers for a solvent of interest must be known before the scale can be used. Furthermore, these empirical constants, by definition, have no physical meaning outside the specific correlation from which they are produced.

Continuum models treat the solvent as a bath into which the solute probe is immersed.[1,2,15] In these models, the bulk solvent properties of dielectric constant and refractive index are used directly. As with the empirical scales described above, the individual solvent–solute interactions are again ignored. Several solvent polarity functions have been developed for use in continuum models while incorporating different levels of approximation.[16–19]

Increased access to computational power has led to an increasing number of more elaborate theoretical models in which solvent can be explicitly included, either by adding one solvent layer or as larger numbers of free solvent molecules.[20,21] However, only after significant effort do these models approach the accuracy of the continuum models. The ability of the continuum models to reproduce observed phenomena suggests that the assumptions implicit in their use are often justified.

In many cases the continuum models have focused on describing the position of the absorption maximum.[1,2,16–19,22–33] Reasonable correlations between the measured and predicted shifts are frequently encountered using these models. Changes in the shape of the absorption spectrum, which often accompany the observed shifts, have received attention only recently.[34–41] This paper expands the current continuum models of solvatochromism to include the analysis of absorption

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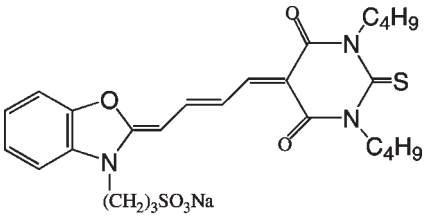
bandshapes as opposed to simply the positions of absorption band maxima. The resulting analysis is significantly more sensitive to changes in the solvent dielectric constant and refractive index than would be observed if changes in band positions alone were used. The aim of this study was to calibrate a solvatochromic probe, specifically merocyanine 540 (M540), to allow the entire absorption spectrum to be predicted in any solvent. Once calibrated, such a probe will allow accurate measurement of both dielectric constant and refractive index of the local environment into which the dye is dissolved.



M540

EXPERIMENTAL

M540 was obtained from Aldrich Chemical and was used without further purification. Pentanenitrile (PCN) and butanenitrile (BCN) were purchased from Aldrich Chemical and were purified by fractional distillation at atmospheric pressure followed by elution through activated alumina before use. Deionized water was used where required. All other solvents, including acetonitrile (ACN), methanol (MeOH), ethanol (EtOH), 2-methoxyethanol (2ME), acetone (A), 2-propanol (2PrOH), 1-butanol (BuOH), octanol (OcOH), tetrahydrofuran (THF) and dioxane (DX), were purchased from EM Science as spectrophotometric grade material and were used as received.

In a typical experiment, a stock solution of M540 (3×10^{-3} M) was prepared in ethanol solution. Aliquots of the stock solution were added to volumetric flasks and the ethanol was evaporated. The desired pure solvents or binary solvent mixtures were then added to yield a final concentration of M540 of 1.5 μM. At this low concentrations of M540, the absorption spectra always obey the Beer–Lambert law, indicating that dimer or higher aggregates are not formed to a significant extent.

Spectroscopic measurements were carried out at room temperature using a Beckman DU-640 UV–visible spectrophotometer. Data files were then transferred to an IBM compatible computer for analysis. Multi-parameter least-squares analysis was accomplished using the Solver function of Microsoft Excel 2000.

RESULTS

Absorption spectra of 1.5 μM M540 solutions in binary mixtures of ACN with 2PrOH were collected and are

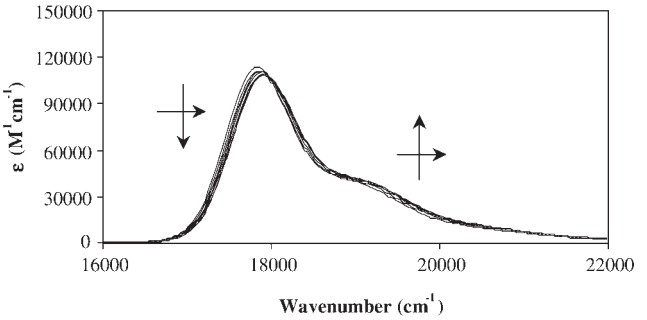


Figure 1. Absorption spectra of M540 in ACN–2PrOH binary solvent mixtures. The arrows indicate the direction of spectral shift with increasing volume percentage of ACN

shown in Fig. 1. Similar data sets were obtained in binary solvent mixtures of DX with EtOH and 2ME with DX. In all cases the M540 absorption spectra consists of a progression of vibronic transitions with two minor bands appearing on the high-energy side of the major band. An additional, minor, low-energy transition was also observed in solvents of very low polarity. This minor absorption was ignored in the fitting process. The spectra were fitted to a sum of three Gaussian functions according to the equation

$$\varepsilon_{\mathrm{OBS}} = \left\{ P_{\varepsilon 1} \times \exp\left[-\left(\frac{P_{S1} - \bar{\nu}}{P_{W1}} \right)^2 \right] \right\} + \left\{ P_{\varepsilon 2} \times \exp\left[-\left(\frac{P_{S2} - \bar{\nu}}{P_{W2}} \right)^2 \right] \right\} + \left\{ P_{\varepsilon 3} \times \exp\left[-\left(\frac{P_{S3} - \bar{\nu}}{P_{W3}} \right)^2 \right] \right\} \quad (1)$$

where $\varepsilon_{\mathrm{OBS}}$ is the observed extinction coefficient at frequency $\bar{\nu}$ in wavenumbers. The spectral parameters $P_{\varepsilon i}$, P_{Si} and P_{Wi} for $i = 1$–3 are the extinction coefficient of band i at its maximum, the position of the band maximum and bandwidth of transition i, respectively. Table 1 gives the least-squares fit parameters obtained along with the dielectric constant and refractive index of the binary solvent system used.[42]

Selected absorption spectra of 1.5 μM M540 in several pure solvents of differing functionality and polarity are shown in Fig. 2. Analysis of the M540 spectra in pure solvents followed a similar procedure to that used in the analysis of the absorptions in binary solvent mixtures. The results of fitting the measured absorption spectra to three Gaussian functions are given in Table 2 along with the dielectric constants and refractive indices of all of the solvents used.[43,44]

DISCUSSION

Examination of the spectra in Figs 1 and 2 shows that negative solvatochromism of the M540 absorption is

Table 1. Gaussian fit parameters for M540 absorption spectra in binary solvent systems

Solvent	D[a]	n[b]	P_{S1}	P_{S2}	P_{S3}	$P_{\epsilon 1}$	$P_{\epsilon 2}$	$P_{\epsilon 3}$	P_{W1}	P_{W2}	P_{W3}
2PrOH–ACN[c]											
20 : 80	32.00	1.348	17878	18855	20598	91735	40813	7612	515	1024	1148
27 : 73	30.81	1.350	17875	18818	20188	91976	36989	8974	515	992	1752
49 : 51	26.64	1.357	17860	18802	19950	90842	34854	10379	512	979	2007
59 : 41	24.91	1.361	17850	18786	20080	92912	36880	9651	511	992	1821
73 : 27	22.75	1.366	17834	18765	20014	93210	36226	9687	508	987	1836
85 : 15	21.05	1.370	17816	18741	19854	93202	34500	10126	503	974	1979
93 : 7	20.16	1.373	17797	18709	19890	95596	35210	9263	500	976	1920
DX–EtOH[c]											
60 : 40	26.64	1.357	17860	18802	19950	90842	34854	10379	512	979	2007
50 : 50	24.91	1.361	17850	18786	20080	92912	36880	9651	511	992	1821
35 : 65	22.75	1.366	17834	18765	20014	93210	36226	9687	508	987	1836
20 : 80	21.05	1.370	17816	18741	19854	93202	34500	10126	503	974	1979
10 : 90	20.16	1.373	17797	18709	19890	95596	35210	9263	500	976	1920
2ME–DX[c]											
60 : 40	8.83	1.408	17756	18680	19742	127041	43633	10829	500	951	1894
70 : 30	10.55	1.406	17768	18699	19878	122315	44241	11126	504	965	1851
75 : 25	11.51	1.405	17773	18704	19897	120175	44609	11514	505	973	1813
80 : 20	12.49	1.404	17778	18757	20541	120951	52915	9338	506	1038	1042
85 : 15	13.52	1.403	17782	18719	20079	119636	47302	11675	508	993	1715
90 : 10	14.62	1.402	17788	18730	20026	122602	48254	12750	509	990	1799
95 : 5	15.77	1.401	17793	18735	20003	118425	46972	12917	510	993	1860

[a] Dielectric constants from Ref 42.
[b] Refractive indices from Ref. 42.
[c] Ratios indicate percentage by volume.

observed. Such shifts in the position of the absorption maximum are indicative of chromophores in which the excited state is less polar than the ground state. Numerous examples of this behavior have appeared.[1–3,30–33] Changes in band shape as a function of solvent polarity are also encountered frequently. As can be observed in Figs 1 and 2, the solvatochroic shift is accompanied by significant changes in the relative intensities of the absorption bands of M540.

What is needed is a simple model function that can be used to correlate all of the spectral changes with solvent properties, such as dielectric constant and refractive index. Several model functions have been developed to describe the spectral shift, but the changes in shape have yet to be exploited fully. The first consideration when choosing model functions was that the observed trends must be accurately reproduced with a minimum number of adjustable parameters. A secondary consideration was that the model function is firmly based on a theoretical model. Several versions of the continuum model have appeared which satisfy both considerations, at least in terms of the positions of the absorption bands.[16–19,22–24] One such function is[24]

$$P_{ji} = P_{0ji} + a_{ji}\left(\frac{n^2-1}{2n^2+1}\right) + b_{ji}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) + c_{ji}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right)^2 \quad (2)$$

Here the bulk solvent properties of dielectric constant (D) and refractive index (n) are correlated with the spectral parameters (P_{ji}), as defined in Eqn (1). The index j is used to specify the extinction coefficient (ε), shift (S) or width (W) while the index i is used to indicate the first, second or third transition. The parameter P_{0ji} represents the limiting value of the shift, width, or extinction coefficient in the absence of solvent. The terms a_{ji}, b_{ji} and c_{ji} are used to describe the influence of solvent on the chromophore. According to continuum models the set of parameters P_{0ji}, a_{ji}, b_{ji} and c_{ji} should be specific to the probe molecule in the absence of specific solvent–solute interactions. Hence, once the probe-specific parameters are known for a particular chromophore, they should be applicable to a wide range of possible solvent environments. In many cases the last term in Eqn (2) has been

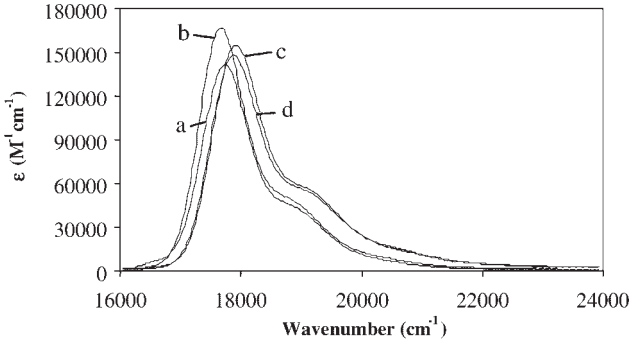


Figure 2. Absorption spectra of M540 in selected pure solvents with differing functionality. Solvents used: (a) OcOH; (b) THF; (c) ACN; (d) EtOH

Table 2. Gaussian fit parameters for M540 absorption spectra in pure solvents

Solvent	D[a]	n[b]	P_{S1}	P_{S2}	P_{S3}	$P_{\varepsilon 1}$	$P_{\varepsilon 2}$	$P_{\varepsilon 3}$	P_{W1}	P_{W2}	P_{W3}
DX	2.21	1.42	17644	18372	20298	89877	47907	3493	457	1407	3293
THF	7.43	1.404	17702	18427	20923	106259	49240	3153	465	1252	1115
OcOH	9.87	1.427	17641	18513	19532	141579	45838	8469	481	984	2135
BuOH	17.35	1.397	17724	18633	19904	136164	48473	10545	488	986	1921
2PrOH	19.29	1.375	17765	18670	19928	136557	49246	9923	490	999	2016
A	20.48	1.357	17836	18774	19750	140462	47684	11248	502	937	1865
PCN	19.9	1.395	17751	18730	20325	146753	51907	5994	492	930	795
BCN	24.3	1.384	17778	18706	19766	133258	46635	8805	490	984	2464
EtOH	24.86	1.359	17845	18788	20076	120993	48707	11993	500	1048	2412
MeOH	32.64	1.326	17986	18967	20396	99846	48924	16184	529	1068	1929
ACN	35.72	1.342	17883	18841	19939	127938	49200	11099	504	1023	2668
Water	78.41	1.332	18450	19682	21413	26979	36026	24704	623	1367	2434

[a] Dielectric constants from Ref 43.
[b] Refractive indices from Ref. 44.

ignored. Significantly better correlations were observed when this term was included in the present study.

Consider the probe characteristic parameters for the shift in absorption, P_{Si}. The parameters, P_{0Si}, a_{Si}, b_{Si} and c_{Si} are related to the magnitudes of the dipole moments of the ground and excited states, in addition to the transition moment and the oscillator strength of the transitions according to the equations[24]

$$a_{Si} = \frac{\mu_g^2 - \mu_e^2}{hca^3} \tag{3}$$

$$b_{Si} = \frac{2\mu_g(\mu_g - \mu_e)}{hca^3} \tag{4}$$

$$c_{Si} = \frac{6\mu_g^2(\alpha_g - \alpha_e)}{hca^6} \tag{5}$$

In reality these parameters may include a contribution due to solvent–solute interactions and care must be exercised when choosing the solvent systems to be examined. Binary mixtures of (relatively) non-interacting solvents should allow a wide range of bulk solvent polarities to be examined without significantly changing the specific solvent–solute interactions that are possible within the first solvent shell. It was expected that the shifts in absorption spectra observed in carefully chosen binary solvent mixtures would conform well to Eqn (2).

The observed shifts in absorption maxima, P_{Si}, for the binary solvent system ACN–2PrOH were analyzed according to Eqn (2) (Fig. 1, Table 1). Least-squares minimization of the difference between the observed and calculated absorption maxima allowed the probe characteristic parameters, P_{0Si}, a_{Si}, b_{Si}, and c_{Si}, for each of the three transitions to be evaluated; a total of 12 parameters were determined.

Using Eqn (2) to fit the DX–EtOH and 2ME–DX data sets also results in excellent agreement between the observed and calculated absorption maxima and two additional sets of probe parameters are determined. If the parameter sets are to be independent of solvent, as continuum theory predicts, all solvent sets should yield identical parameter values. Unfortunately, comparisons among the three sets of probe-specific parameters revealed significant variation from one solvent system to the next. The observed variation may be the result of differences in specific solvent–solute interactions within these binary solvent mixtures. Alternatively, as will be described below, excessive degrees of freedom may be present in the fitting function and the probe-specific values may not have converged to their true values during the fitting procedure.

To establish a general set of probe characteristic values, it was assumed that the solvent–solute interactions were indeed negligible in these solvent systems and all three binary data sets were fitted to Eqn (2) simultaneously. The resulting, general set of probe-characteristic parameters is again different from the previous three sets. However, the correlation coefficients for the individual data sets are not decreased significantly when the general set of parameters is assumed. Correlation plots of the calculated P_{Si} values, obtained using the general set of characteristic probe values, and the observed P_{Si} values, obtained from the Gaussian fits for each vibronic transition, are shown in Fig. 3.

Equations (3)–(5) were then used to calculate the change in dipole moment, $\Delta\mu = \mu_g - \mu_e$, and the change in polarizability, $\Delta\alpha = \alpha_g - \alpha_e$ of M540 using the general set of parameters. The values obtained for the first transition in the M540 absorption were $\Delta\mu = 0.46$ D and $\Delta\alpha = 197$ Å.[3] These values are in good agreement with the published values of $\Delta\mu \approx 0.2$–1.1 D and $\Delta\alpha \approx 200$ Å.[3, 45–48] The general parameters obtained from the analysis of the second absorption band yield similar results for $\Delta\mu$ and $\Delta\alpha$, but the general parameters obtained based on the third, and weakest, absorption band do not. Apparently, significant freedom in the fitting function is indeed a problem and the general parameters have probably not yet fully converged. Nevertheless, the

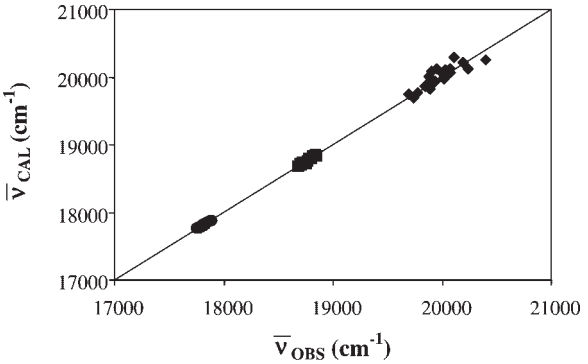


Figure 3. Correlation plot of the calculated and observed absorption maximum for the first (●), second (■) and third (◆) absorption bands of M540 in binary solvent mixtures

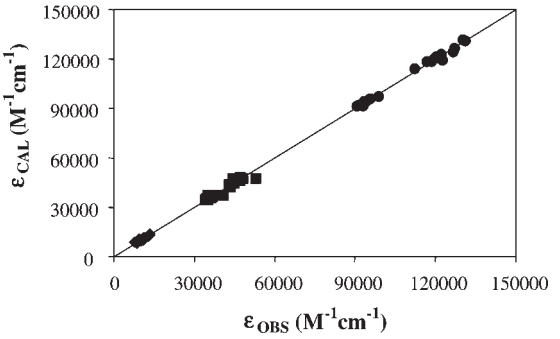


Figure 4. Correlation plot of the calculated and observed extinction coefficients for the first (●), second (■) and third (◆) absorption bands of M540 in binary solvent mixtures

general set of parameters was adopted as the best representative values for use in Eqn (2) to predict the frequencies of the three maxima in the M540 absorption spectrum based solely on the dielectric constant and refractive index of the solvent. This final, general set of probe characteristic parameters is collected in Table 3.

Examination of the spectra in Figs 1 and 2 shows clearly that the absorption bandshapes also respond to changes in solvent polarity. Several theoretical models have been proposed which reproduce spectral bandshapes surprisingly well.[34–41] In general, these models require knowledge of the solvent reorganization energies, parameters usually obtained by the fitting procedure. Although it is possible to estimate the reorganization energies, which are again based on the solvent D and n, these estimates do not allow the spectral data to be reproduced with the required accuracy to be useful to the present study. Therefore, an alternative approach was required and Eqn (2) was adopted for use in correlating the observed changes in extinction coefficient. Although there is no firm theoretical basis to believe that Eqn (2) should be use for this purpose, its use is not completely unjustified. The transition energy (shift) and extinction coefficient (height) are both related to $\Delta\mu$ and $\Delta\alpha$.[1,2] The fact that a reasonable correlation between the observed and predicted ε_{max} values does occur was viewed as sufficient justification for the stated purpose of this paper. The $P_{\varepsilon i}$ values obtained from the least-squares minimization of the difference between the extinction coefficients obtained from the spectral fit parameters (Table 1) for all three binary solvent systems fitted simultaneously and those predicted based on application of Eqn (2) are also collected in Table 3. Correlation plots of the calculated and observed extinction coefficients are shown in Fig. 4.

Table 3. Probe-specific parameters for M540 obtained using the binary solvent mixtures

	i		
Parameter	1	2	3
P_{0Si}	19322	19071	28939
a_{Si}	−8305	−3361	−43336
b_{Si}	−50.8	−658	3933
c_{Si}	69.9	1719	−8311
$P_{0\varepsilon i}$	−358419	72411	28126
$a_{\varepsilon i}$	2134864	−141160	−121515
$b_{\varepsilon i}$	1065	39055	−5561
$c_{\varepsilon i}$	186205	−62638	19910
P_{0Wi}	499	969	1658

The last parameters to be determined are the spectral bandwidths, P_{Wi}. Comparisons among the data collected in Table 1 suggest that the bandwidths do not change significantly with solvent polarity. A plot of the observed bandwidths versus any form of the solvent polarity function results in a scatter diagram with no discernable trends. The average values for the transition widths for each of the three transitions were assigned to the three P_{0Wi} values and a_{Wi}, b_{Wi} and c_{Wi} were assumed to be zero. These values are also collected in Table 3.

With the complete set of probe characteristic parameters at hand (Table 3), the entire absorption spectrum of M540 can be simulated based solely on the bulk dielectric constant and refractive index of the solvent as the only adjustable parameters. Conversely, and perhaps more importantly, evaluating the absorption spectrum of M540 in any solvent using the 27 spectral parameters collected in Table 3 as fixed values should allow the dielectric constant and refractive index of the solvent to be estimated. To test the accuracy with which these parameters could be used to predict the bulk solvent properties, the absorption spectra of M540 in several solvents with a range of polarities and functional groups were collected and analyzed.

Consider the absorption spectrum of M540 in butanol shown in Fig. 5. The M540 absorption spectrum has the same general features as those observed in the binary solvent mixtures and can also be fitted accurately using three Gaussian functions (Table 2). The general probe parameters collected in Table 3 were used to evaluate the absorption spectrum for initial guesses of D and n and the square of the difference between the calculated and observed spectra was computed. The least-squares summation was then weighted using the differences between

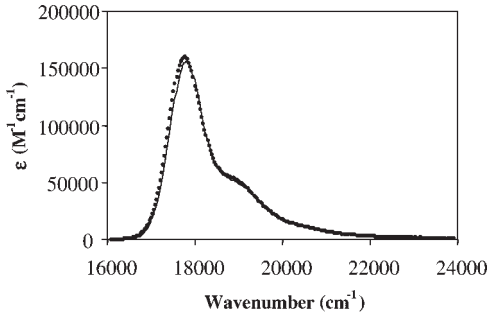


Figure 5. Plot of the observed absorption spectrum of M540 in butanol solvent (•). The line indicates the predicted spectrum obtained using the probe specific parameters and the predicted *D* and *n* of 17.93 and 1.388, respectively (see text)

the predicted $P_{\varepsilon i}$ and P_{Si} with those obtained directly from the Gaussian fitting procedure (Table 2) according to the equation

$$WSS = \left(\left\{ \sum_{i=1}^{3} \left[(P_{Si})_{\mathrm{CALC}} - (P_{Si})_{\mathrm{OBS}} \right] \right\} \times \left\{ \sum_{i=1}^{3} \left[(P_{\varepsilon i})_{\mathrm{CALC}} - (P_{\varepsilon i})_{\mathrm{OBS}} \right] \right\} \right)^2 \times \left[OD(\nu_l)_{\mathrm{CALC}} - OD(\nu_l)_{\mathrm{EXP}} \right]^2 \quad (6)$$

The assumed values of *D* and *n* were adjusted to minimize the absolute value of the weighted least-squares summation (*WSS*). For the M540 absorption spectrum in butanol this procedure resulted in the calculated spectrum shown in Fig. 5 and predicted values of *D* and *n* of 17.93 and 1.388. These values are in excellent agreement with the literature values[43,44] of 17.35 and 1.397, respectively.

The absorption spectra of M540 in numerous pure solvents were analyzed using a similar procedure and the values obtained are given in Table 4 along with the literature values for comparison. Satisfactory agreement

Table 4. Dielectric constants and refractive indices of pure solvents determined using bandshape analysis of the M540 absorption

Solvent	$\varepsilon_{\mathrm{CAL}}$	$\varepsilon_{\mathrm{LIT}}$[a]	n_{CAL}	n_{LIT}[b]
DX	2.2	2.21	1.420	1.420
THF	7.41	7.43	1.405	1.404
Octanol	9.91	9.87	1.423	1.427
Butanol	17.93	17.35	1.388	1.397
2-PrOH	19.99	19.29	1.377	1.375
Pentanenitrile	19.58	19.9	1.393	1.395
Acetone	19.22	20.48	1.384	1.357
Butanenitrile	24.07	24.3	1.365	1.384
EtOH	24.42	24.86	1.345	1.359
Methanol	35.34	32.64	1.302	1.326
ACN	36.53	35.72	1.342	1.342

[a] Dielectric constants from Ref. 43.
[b] Refractive indices from Ref. 44.

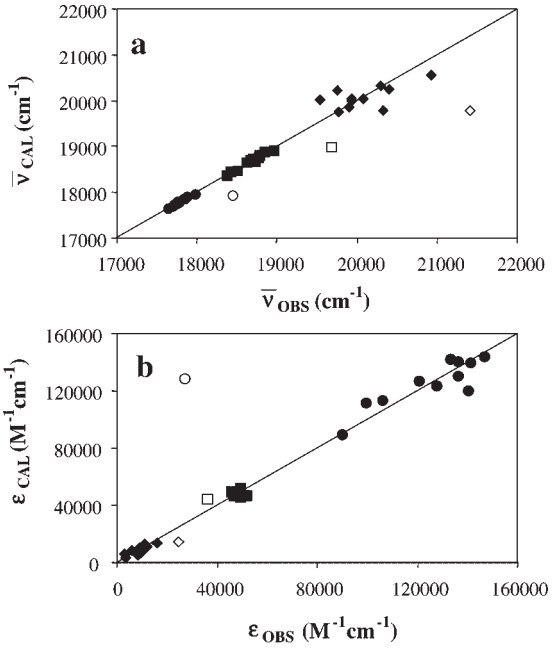


Figure 6. Correlation plots for the observed and calculated absorption maximum (a) and extinction coefficients (b) for the first (•), second (■) and third (◇) absorption bands of M540. The three absorption bands for water are shown using ○, □ and ◆ for the first, second and third absorption bands, respectively

between the measured and literature values was obtained for all solvents examined, with the exception of water. The correlation plots of the calculated versus observed absorption maxima and extinction coefficients are shown in Fig. 6. These plots were not significantly improved if the ketones and nitriles or alcohols were considered separately.

It is surprising that the predicted solvent properties and the literature solvent properties are in general agreement for the different classes of solvents examined. Clearly, the strength and nature of the solvent–solute interactions possible in alcohols, including methanol, would be expected to be significantly different to those occurring in the nitrile or ketone solvents and continuum models ignore the possibility of direct solvent–solute interactions. The fact that a single set of parameters is able to describe the absorption spectrum of M540 in several classes of solvents suggests that the influence of solvent-solute interactions on the absorption spectrum is at least constant over all solvents studied if they are not altogether insignificant.

The predicted spectrum of M540 in water deviates significantly from that expected based on all of the other solvents studied. There are no values of *D* and *n* that can be used with the general solvent parameter set (Table 3) to account for the observed M540 spectrum in water. Apparently, in highly interacting solvents, such as water, solvent–solute interactions may not only be significant but may also cause a change in the nature of the chromophore in ways that continuum models cannot predict.

It is of interest to see whether the current technique of simulating the absorption spectrum of M540 can be of use with microheterogeneous samples where the bulk properties are not known. In these cases multiple binding environments may result in broadening of the absorption spectrum because of inhomogeneity in the binding environment. Simulating the absorption spectrum, as described here, would have the added advantage of being able to identify multiple binding environments simultaneously. Studies of this nature are under investigation.

CONCLUSION

Continuum models have been expanded to allow the entire absorption spectrum of a solvatochromic dye to be predicted based on the dielectric constant and refractive index of the bulk solvent. A single set of probe-specific parameters was used to determine the solvent properties of several classes of solvents with a wide range of polarities and functional groups. These findings indicate that specific solvent–solute interactions, which are ignored in continuum models, must be constant, if not insignificant, for all of the solvent studied, with the exception of water. It is notable that no values of the dielectric constant or refractive index, under any conditions, could reproduce the absorption spectrum of M540 in water.

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