Empirical treatment of solvent–solute interactions: medium effects on the electronic absorption spectrum of β-carotene

T. Abe,[1] J.-L. M. Abboud,[2]* F. Belio,[3] E. Bosch,[4] J. I. Garcia,[3] J. A. Mayoral,[3] R. Notario,[2] J. Ortega[4] and M. Rosés[4]

[1]Department of Chemistry, Faculty of Science, Tohoku University, Kawauchi, Aoba-ku, Sendai 980, Japan
[2]Instituto de Química Física 'Rocasolano,' CSIC, c/Serrano 119, E-28006 Madrid, Spain
[3]Departamento de Química Organica e Instituto de Ciencia de Materiales de Aragón, CSIC, Universidad de Zaragoza, E-50009 Zaragoza, Spain
[4]Departament de Química Analítica, Avda. Diagonal 647, E-08028 Barcelona (Catalonia), Spain

ABSTRACT: Solvent effects on the wavenumber of the maximum of the longest wavelength electronic absorption band of all-*trans*-β-carotene were determined in 34 solvents. Together with results from previous studies, a data set for 51 solvents, mostly non-hydrogen bond donors, was constructed. This information was analyzed in terms of reaction field models and also showed its value for correlation purposes when used either alone or in combination with standard empirical solvent polarity–polarizability scales. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Solvent–solute interactions; β-carotene; electronic absorption spectrum; solvent effects

INTRODUCTION

Empirical solvent scales[1] are intended to provide quantitative measures of solvent–solute van der Waals interactions. In the absence of specific effects such as hydrogen bonding (HB) and/or charge transfer, the fundamental contributions to these interactions have electrostatic and dispersive origins. A number of theoretical treatments[2] have been developed that quantitatively link these effects to properties of the bulk solvents, notably the refractive index n and relative permittivity of the bulk solvent, ε_r (formerly known as dielectric constant). Possibly the simplest among these models is that by Onsager[3] and Kirkwood.[4] There, the solute molecule is assumed to be a sphere of radius a with a point dipole μ located at the center. The solute dipole interacts with the molecules of the solvent, which in turn create an electric field, the reaction field $\mathbf{E_R}$. In the case of a non-polarizable solute embedded in an isotropic solvent, this theory leads to the equation

$$\mathbf{E_R} = 2(\varepsilon_r - 1)/(2\varepsilon_r + 1)(\mu/a^3) \tag{1}$$

The concept of reaction field is extremely valuable, as $\mathbf{E_R}$ can be related to a number of solvent effects, including UV–Visible,[2] fluorescence,[2c,5] IR[6] and NMR[7] frequency shifts, and free energies of transfer between

solvents.[4,8] It therefore rationalizes the link between these seemingly unrelated phenomena. This model also predicts a correlation between medium effects and the permittivity function $\phi(\varepsilon_r)$, defined by the equation

$$\phi(\varepsilon_r) = (\varepsilon_r - 1)/(2\varepsilon_r + 1) \tag{2}$$

If the solute polarizability is taken into account, the functional dependence between $\mathbf{E_R}$ and μ becomes more complex. It is worth mentioning that, in the case where the refractive index of the solvent, n, equals $2^{1/2}$ (a reasonable average value for many solutes), the appropriate permittivity function takes the form

$$g(\varepsilon_r) = (\varepsilon_r - 1)/(\varepsilon_r + 1) \tag{3}$$

These electrostatic interactions are usually only a small fraction of the total solvent–solute van der Waals interactions, the leading term more frequently being London's dispersion forces.[9] Extension of reaction field theory to these interactions predicts[10] an approximate relationship between dispersion-originated solvent effects and the function of the refractive index of the solvent $\phi(n^2)$:

$$\phi(n^2) = (n^2 - 1)/(2n^2 + 1) \tag{4}$$

These magnitudes can be used for the study of $\sigma(S)$, the frequency of the solvatochromic band of an indicator in solvent S. For example, the widely used Ooshika–Bayliss–McRae formalism[2] leads to

$$\sigma(S) = \sigma(g) + \Delta\sigma_d + \Delta\sigma_{ind} + \Delta\sigma_{el} \tag{5}$$

where $\Delta\sigma_d$, $\Delta\sigma_{ind}$ and $\Delta\sigma_{el}$ represent dispersion, induc-

Table 1. Wavenumber of the longest wavelength absorption maximum in the UV–visible spectrum of -carotene (σ_{max}, in cm^{-1}), wavenumber of the C=O stretching vibration of butanone ($\nu_{C=O}$, in cm^{-1}), wavenumber of the 0–0 band for the longest wavelength absorption in the UV–visible spectrum of all-*trans*-1,3,5,7-octatetraene (σ_{0-0}, in cm^{-1}), refractive index (n), relative permittivity (ε_r) and solvatochromic parameters E_T^N, π^*_{OMe} and SPP^N for the gas phase and 51 solvents

No.	Solvent	$\sigma_{max}{}^a$	n^c	$\varepsilon_r{}^f$	$E_T^{N\ g}$	$\pi^*_{OMe}{}^h$	$SPP^{N\ i}$	$\nu_{C=O}{}^j$	$\sigma_{0-0}{}^k$
—	Gas phase		1.000	1.000	−0.111	−1.23	0	1742.0	35523
Perfluorinated hydrocarbons									
1	Hexafluorobenzene	22165	1.377	2.05	0.108	0.27	0.629		
Cyclic and acyclic non-aromatic hydrocarbons									
2	Cyclohexane	22008[b]	1.426[d]	2.024[d]	0.006	0.00	0.557	1726.1	
3	Methylcyclohexane	22030[b]	1.423[d]	2.020[d]			0.563		
4	*t,t,c*-1,5,9-Cyclododecatriene	21603	1.507	2.41		0.30			
5	Perhydrofluorene	21628	1.502	2.31		0.15			
6	*n*-Pentane	22331[b]	1.358[d]	1.841[d]	0.009	−0.15	0.507		33180
7	Isopentane	22364[b]	1.354[d]	1.828[d]	0.006	−0.15	0.479		
8	3-Methylpentane	22251	1.377[d]	1.895[d]					
9	*n*-Hexane	22232	1.375[d]	1.886[d]	0.009	−0.11	0.519	1727.0	33110
10	*n*-Nonane	22070[b]	1.405[d]	1.970[d]	0.009		0.552		
11	*n*-Dodecane	21988[b]	1.422[d]	2.002[d] (30 °C)	0.012	−0.01	0.571		
12	*n*-Hexadecane	21905[b]	1.435[e]	2.05[e]			0.578		32808
Aromatic hydrocarbons									
13	Benzene	21575[b]	1.501[d]	2.274[d] (25 °C)	0.111	0.55	0.667	1719.0	32435
14	Toluene	21598	1.497	2.43	0.099	0.49	0.655	1717.7	
15	1,4-Dimethylbenzene (*p*-xylene)	21673	1.496[d]	2.270[d]	0.074	0.45	0.617		
16	1-Methylnaphthalene	21160	1.618[d]	2.915[d]	0.142	0.78			
17	1,2,3,4-Tetrahydronaphthalene (tetralin)	21434[b]	1.541[d]	2.773[d]	0.086		0.668		
Halogenated compounds									
Non-aromatic									
18	Dichloromethane	21650	1.424	9.02	0.309	0.73	0.876	1712.7	32385
19	Chloroform	21576[b]	1.446	4.89	0.259	0.69	0.786	1710.3	32550
20	Tetrachloromethane	21630[b]	1.460	2.30	0.052	0.21	0.632	1721.0	
21	1,1-Dichloroethane	21930	1.416[d]	10.0[d] (18 °C)	0.269				
22	1,2-Dichloroethane	21580	1.445	10.74	0.327	0.73	0.890		
23	1,1,1-Trichloroethane	21744	1.438	7.33	0.170	0.44			
24	Iodoethane	21413	1.513	7.77		0.65			
25	Diiodomethane	20475	1.741[d]	5.316[d] (25 °C)	0.179	1.00			
Aromatic									
26	Fluorobenzene	21697	1.465	5.55	0.194	0.59	0.769		
27	Chlorobenzene	21409	1.524	5.74	0.188	0.68	0.824		
28	Iodobenzene	20999[b]	1.620	4.75	0.170	0.84			
Nitriles									
29	Acetonitrile	22070	1.344[d]	35.94[d] (25 °C)	0.460	0.66	0.895	1714.1	
Ethers									
30	Diethyl ether	22207	1.352	4.42	0.117	0.24	0.694	1721.2	
31	1,4-Dioxane	21725	1.422	2.27	0.164	0.49	0.701		
32	Tetrahydrofuran (THF)	21844	1.406	7.47	0.207	0.55	0.838	1716.2	
33	Diisopropyl ether	22183	1.367	4.04	0.105	0.19			
Acyl compounds									
Ketones									
34	Acetone	22046	1.359	21.36	0.355	0.62	0.881		
35	Butan-2-one	21983	1.379	18.85	0.327	0.60	0.881	1717.1	
Esters, lactones									
36	Propylene carbonate	21734	1.421	62.93	0.472	0.83	0.930		
37	Ethyl acetate	22046[b]	1.372	6.03	0.228	0.45	0.795	1717.0	
Disubstituted amides									
38	*N,N*-Dimethylformamide (DMF)	21622[b]	1.430	37.06	0.386	0.88	0.954	1712.1	
39	*N,N*-Dimethylacetamide (DMA)	21642	1.438	38.30	0.377	0.85	0.970	1711.5	
Sulfoxides									
40	Dimethyl sulfoxide (DMSO)	21372	1.479	46.71	0.444	1.00	1.000	1710.6	
Pyridines									
41	Pyridine	21346[b]	1.509	13.22	0.302	0.87	0.922	1714.0	

Table 1. *Continued.*

No.	Solvent	σ_{max} [a]	n [c]	ε_r [f]	E_T^{N} [g]	π^*_{OMe} [h]	SPP^{N} [i]	$\nu_{C=O}$ [j]	σ_{0-0} [k]
Tertiary amines									
42	Triethylamine	22041	1.401	2.45	0.043	0.09	0.617		
43	*N,N*-Dimethylaniline	21263	1.559[d]	4.91[d]	0.179	0.76			
Nitro compounds									
44	Nitromethane	21844	1.381	36.16	0.481	0.75	0.907	1711.0	
Miscellaneous									
45	Hexamethylphosphoramide (HMPA)	21592	1.458	29.00	0.315	0.87	0.932		
46	Carbon disulfide	20730[b]	1.627[d]	2.643[d]	0.065	0.51		1719.8	
Hydrogen bond donors									
Primary and secondary amines									
47	Diethylamine	22168	1.386	3.92	0.145	0.35			
48	Aniline	21039	1.585	7.16	0.420	1.08			
49	*N*-Methylaniline	21155	1.571[d]	5.90[e]	0.364				
Alcohols									
50	Methanol	22247	1.328[d]	32.66[d]	0.762	0.56	0.857		33190
51	Ethanol	22134	1.361[d]	24.55[d]	0.654	0.50	0.853		

[a] This work unless stated otherwise.
[b] From Ref. 27a.
[c] Refractive index of the medium, measured at 20.0 °C, unless stated otherwise; values taken from Ref. 13, unless stated otherwise.
[d] Values taken from Ref. 25.
[e] Values taken from Ref. 26 and the original references cited therein.
[f] Relative permittivity of the medium, measured at 20.0°C, unless stated otherwise; values taken from Ref. 13, unless stated otherwise.
[g] From Ref. 1b.
[h] From Ref. 13.
[i] From Ref. 18.
[j] From Ref. 27b.
[k] From Ref. 33.

tion and dipole–dipole components of van der Waals interactions and are given by

$$\Delta\sigma_d = A''(n^2 - 1)/(2n^2 + 1) \qquad (6)$$

$$\Delta\sigma_{ind} = B'(n^2 - 1)/(n^2 + 1) \qquad (7)$$

$$\Delta\sigma_{el} = C[(\varepsilon_r - 1)/(\varepsilon_r + 1) - (n^2 - 1)/(n^2 + 1)] \qquad (8)$$

The functions $(n^2 - 1)/(n^2 + 1)$ and $(n^2 - 1)/(2n^2 + 1)$ [and also the classical Clausius–Mossotti function $(n^2 - 1)/(n^2 + 2)$] are very strongly correlated[11] over the range $1 \leq n \leq 2$. This is why we shall use equations (9) and (10) for the analysis of experimental data, given the impossibility of achieving a proper separation of A'' and B' by correlation analysis methods:

$$\sigma(S) = (A' + B')(n^2 - 1)/(n^2 + 1) + C[(\varepsilon_r - 1)/$$
$$(\varepsilon_r + 1) - (n^2 - 1)/(n^2 + 1)] + D \qquad (9)$$

$$\sigma(S) = A(n^2 - 1)/(n^2 + 1) + C[(\varepsilon_r - 1)/$$
$$(\varepsilon_r + 1) - (n^2 - 1)/(n^2 + 1)] + D \qquad (10)$$

The spirit of some of the criteria set forth by Koppel and Palm[11] and Palm and Palm[12] is useful at this point: on the basis of the theoretical methods indicated above, we consider, as done previously,[13] that the non-specific contribution to medium effects on $\sigma(S)$ can be expressed

as a linear combination of the functions $[g(\varepsilon_r) - f(n)]$ and $f(n)$:

$$[g(\varepsilon_r) - f(n)] = (\varepsilon_r - 1)/(\varepsilon_r + 1) - (n^2 - 1)/(n^2 + 1) \qquad (11)$$

$$f(n) = (n^2 - 1)/(n^2 + 1) \qquad (12)$$

Thus, from the standpoint of correlation analysis and as a first approximation, solvatochromic scales can generally be analyzed (in the absence of specific interactions) as linear combinations of $f(n)$ and $[g(\varepsilon_r) - f(n)]$. Let *SC* be any such scale. Then, the equation

$$SC = SC_0 + a[g(\varepsilon_r) - f(n)] + bf(n) \qquad (13)$$

holds, where SC_0 is the value of *SC* for the gas phase and a and b are constants. Slightly different forms of this equation apply whenever the reference medium is not the gas phase.

Analyses of this kind have been carried out[13,14] on the π^* scale of dipolarity–polarizability[15], and also on E_T^N,[1b,16] π^*_{azo},[17] SPP^N[18] and S'.[1a,19] They show[13,14] that the ratio a/b is a characteristic property of each scale and varies between very wide limits. In this respect, Laurence *et al.*[20] have shown that, in the absence of HB interactions, the main difference between π^* and $E_T(30)$ lies in their widely different responses to solvent

polarizability effects [as measured by $f(n)$ and cognate functions].

Some years ago, Abe[21a] drew attention to the fact that most solvent polarity scales available at that time were based on solvatochromic shifts undergone by electronic transitions of solutes endowed with large dipole moments in either or both the ground and the excited states. This prompted him to investigate the possibility of building a scale based on electronic transitions of solutes characterized by small or zero dipole moments in both the ground and the excited states. This was a means of quantifying effects essentially determined by dispersive interactions.[9] As a 'molecular probe,' naphthalene was selected. The electronic transition was the ^1L_b band, located in the near-UV region and known to be solvent sensitive.[22] Solvent-induced frequency shifts of this band were found to correlate to a very high degree of precision with medium effects on the ^1L_b band of anthracene and with the maximum of the longest wavelength absorption band of β-carotene. The new scale, $\pi*_2$, was therefore based on the shifts of the ^1L_b band of naphthalene (the origin being taken as $\pi*_2 = 1.00$ for cyclohexane) and extended to a substantial number of solvents through the abovementioned correlations. This scale was shown to be most appropriate for the treatment of solvent-induced shifts of a variety of conjugated hydrocarbons. Linear combinations of $\pi*_2$ with $\pi*$ proved very satisfactory at analyzing other spectroscopic and reactivity data involving polar species.

At this point it seems that the usefulness of the $\pi*_2$ scale has been demonstrated, but there is still room for new developments. Thus, as in the case of the $\pi*$ scale, it is possible to investigate the behavior of a single 'molecular probe,' in order to have a well defined single reference, even at the cost of magnifying any effects originating, for example, in the size and shape of the indicator.[13,23] The longest wavelength absorption in the UV–visible spectrum of β-carotene seems an interesting possibility, as it is located in a spectral region that is well removed from the cut-off of many common solvents. Furthermore, the sensitivity of this band to medium effects is very substantial. a consequence of the polarizability of the β-carotene molecule in the excited state being much larger than in the ground state (as has been found to be the case for lycopene and all-*trans*-retinal[21b]). Here, we report the results of a study of the influence of 52 solvents on the frequencies of this absorption band. Of these, 34 values were determined for the first time. Solvents were chosen in order to span a wide range of n and ε_r values. Also, we tried to include a wide variety of functionalities and of molecular sizes and shapes.

EXPERIMENTAL

All-*trans*-β-carotene was a Merck 'for biochemistry'

product, crystallized from benzene and methanol. Solvents were of spectroscopic grade or of the highest commercial purity available. They were dried over molecular sieves and carefully distilled prior to use.

The solutions of β-carotene were 6×10^{-6} M. Matched 1 cm silica windows cells were used throughout.

A Perkin-Elmer Lambda 19 UV–visible spectrophotometer was used to obtain the spectra. The temperature of the cells was kept constant at $25.0 \pm 0.1\,°C$ by means of a Perkin-Elmer C570-070 Peltier digital controller. Separate checks of the results were carried out by means of a Beckman DU-7 spectrophotometer and an external bath. In both cases, the instruments were calibrated with holmium glass filters. In the case of the first spectrophotometer, data acquisition and treatment and the search of the absorption maxima were carried out with both the standard software and with software developed in our laboratories. In the case of the Beckman DU-7 spectrophotometer, data acquisition was carried out with the program DUMOD.[24] Smoothing of the spectra and determination of the absorption maxima were performed using our software. It was established that the absorption maxima obtained with two different solutions, prepared on different dates and examined with both spectrophotometers, were coincident to within ± 0.1 nm.

RESULTS AND DISCUSSION

The experimental results are presented in Table 1. The frequencies of the absorption maximum, σ_{max} are given in cm^{-1}.

Because of their usefulness for the discussion, the corresponding refractive indices (n), and relative permittivities (ε_r) at 25 °C of the various solvents together with the values of E_T^N, $\pi*_{OMe}$ and SPP^N are also given. E_T^N is the 'normalized' value of the $E_T(30)$ parameter, as defined by Reichardt.[1b,1e,16] $\pi*_{OMe}$ is the value of Kamlet–Abboud–Taft's $\pi*$[15] as determined on the basis of solvatochromic effects on the longest wavelength absorption maximum of 4-nitroanisole[13] and SPP^N is the 'normalized' value of the SPP parameter, recently defined by Catalán *et al.*[18] as the difference in the solvatochromic shifts undergone by the longest wavelength absorption bands of 2-(dimethylamino)-7-nitrofluorene and 2-fluoro-7-nitrofluorene.

Non-dipolar solvents

β-Carotene is an all-*trans* polyene. In agreement with the theoretical treatments of Liptay[28] and with the experimental results of Feichtmayr *et al.*[29] as discussed by Abe,[21a] the frequency of the absorption maximum of the longest wavelength transition is primarily affected by dispersive interactions, which induce bathochromic shifts. Thus, as indicated in the Introduction, a linear
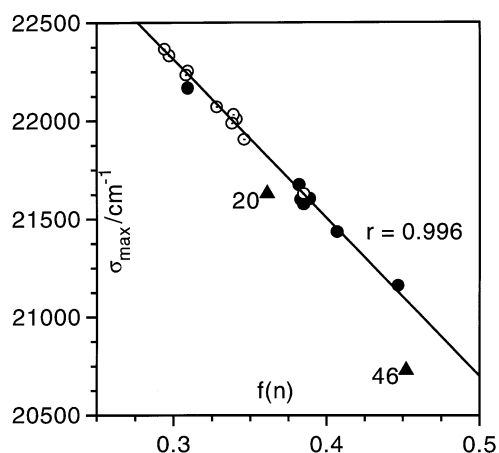
Figure 1. σ_{max} vs $f(n)$. Open circles, aliphatic and alicyclic hydrocarbons; closed circles, **4** and aromatic hydrocarbons

Figure 3. SPP^N vs $f(n)$. Open circles, aliphatic and alicyclic hydrocarbons; closed circles, aromatic solvents

relationship is predicted between σ_{max} and $f(n)$, at least for solvents devoid of permanent dipole moments (for these materials, $\varepsilon_r \approx n^2$). Indeed, using the data in Table 1, the following excellent linear relationship is obtained for the hydrocarbon solvents **1–17**:

$$\sigma_{max}(cm^{-1}) = 24678(63) - 7.94(0.18) \times 10^3 f(n) \tag{14}$$

($n = 17$, $r = 0.996$, SD = 31 cm^{-1}; standard deviations in parentheses)

The intercept of equation (14), 24678 cm^{-1}, can be taken as a reasonable estimate of the value of σ_{max} in the gas phase, since the low volatility of β-carotene does not allow the experimental determination of this value.

Equation (14) supports the theoretical predictions, and also Abe's results. It is worth noting that the frequencies determined in aromatic solvents (including the very feebly polar toluene and 1-methylnaphthalene) comply
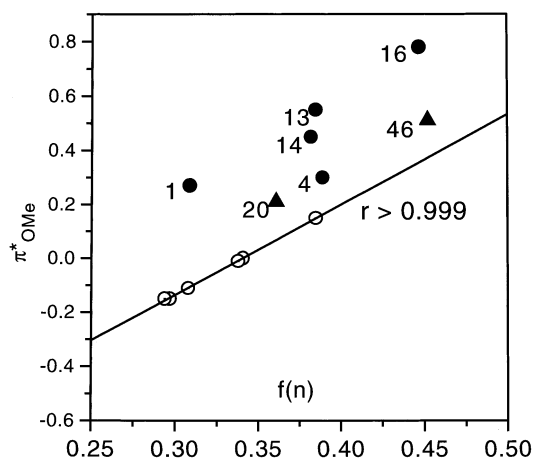
well with this equation. On the other hand, the σ_{max} values for CCl_4 and CS_2 are off the line defined by this equation. This point will be examined later. These results are displayed in Fig. 1.

For the purpose of comparison, the following results were obtained with the available data for the various scales selected.

(a) E_T^N. The values for aliphatic and alicyclic hydrocarbons are essentially independent of $f(n)$, in agreement with Laurence et al.[20] As they pointed out, this probably originates in the compensation of the opposing effects of dispersion (a systematic bathochromic shift[30] and polarity (hypsochromic effect). Non-polar or weakly polar aromatic hydrocarbons, and also CCl_4, and CS_2, have modest but significant effects on E_T^N. This might reflect the influence of multipolar interactions.

(b) π^*_{OMe} (Fig. 2). An excellent linear relationship between π^*_{OMe} and $f(n)$ exists that applies to aliphatic and acyclic hydrocarbons, in addition to the gas

Figure 2. π^*_{OMe} vs $f(n)$. Open circles, aliphatic and alicyclic hydrocarbons; closed circles, **4** and aromatic solvents

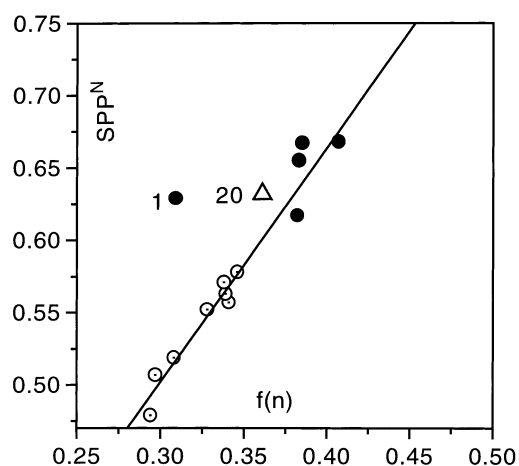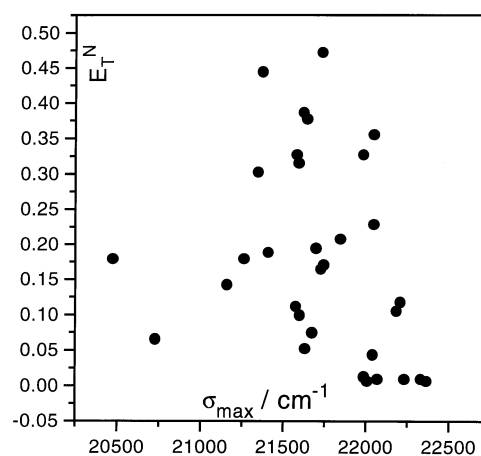**Figure 4.** E_T^N vs σ_{max} The plot does not include the data points for **50** and **51**

phase.[13,31] This plot also shows that CCl_4, and CS_2 and weakly, dipolar or apolar aromatics have substantially enhanced π^*_{OMe} values. This behavior is similar to that of σ_{max} and reflects the importance of multipolar interactions and also (perhaps) more specific interactions (such as donor–acceptor effects).[13] In the particular case of the π^* scale, this effect is corrected by means of the $d\delta$ formalism.[8,13]

(c) SPP^N (Fig. 3). As shown in this plot, there is a fair correlation between SPP^N and $f(n)$ for aliphatic and alicyclic hydrocarbons. CCl_4 and apolar aromatic solvents deviate significantly. Hexafluorobenzene (**1**) is very far from the line, suggesting some specific interactions with the probes.[18]

Dipolar solvents

From the data given in Table 1, 46 solvents were selected and their σ_{max} values treated by means of equation (13). Only **50** and **51** (strong hydrogen bond donors) and **20**, **31** and **46** were excluded from the treatment {for the latter, symmetry imposes $[g(\varepsilon_r) - f(n)] = 0$, while multipolar interactions can be very important}. The following equation was obtained:

$$\sigma_{max} = -8.07(0.18) \times 10^3 f(n) - 485(37)[g(\varepsilon_r) - f(n)]$$

$$+24729(66) \tag{15}$$

$$(n = 46, r = 0.990, SD = 58 \text{ cm}^{-1})$$

Note that the coefficients of $f(n)$ and the independent term in equations (14) and (15) agree well within the limits of uncertainty. This shows the 'robust' character of the correlations. This equation contains data for solvents **18**, **19**, **21**, **29**, **44**, **47**, **48** and **49**. These species are weak hydrogen bond donors. They depart from the behavior described by equation (15) by amounts ranging between one and two standard deviations. These differences are relatively modest and clearly indicate that hydrogen bonding interactions involving β-carotene as a hydrogen bond acceptor are not very large [if equation (15) is applied to σ_{max} values in **50** and **51**, larger deviations appear. A broader study of the influence of hydrogen bonding acidity on the solvatochromism of β-carotene is in progress]. Excluding these data, and also the datum for **22** (because of its well known conformational characteristics[32], we obtain the equation

$$\sigma_{max} = -8.03(0.16) \times 10^3 f(n) - 465(32)[g(\varepsilon_r)$$

$$-f(n)] + 24717(60) \tag{16}$$

$$(n = 37, r = 0.993, SD = 49 \text{ cm}^{-1})$$

The ratio a/b, as defined in equation (13), equals 0.061, which can be compared with the values of 0.274 for π^*_{OMe}[13] and 0.411 for SPP^N.[14] As indicated earlier, the

contribution of $f(n)$ to E_T^N is barely significant ($r = 0.08$ for 189 solvents[14]). One is then led to expect a very poor correlation between σ_{max} and E_T^N. Figure 4 shows that this is indeed the case ($r = 0.26$). It therefore seems possible to express scales such as π^*_{OMe} and SPP^N in terms of linear combinations of σ_{max} and E_T^N. Equations (17) and (18) are then obtained.

$$\pi^*_{OMe} = -384(36) \times 10^{-6}\sigma_{max}$$

$$+1.81(0.11)E_T^N + 8.47(0.79) \tag{17}$$

$$(n = 21, r = 0.984, SD = 0.07)$$

Equation (17) involves all the available data for aliphatic and alicyclic, non-hydrogen bond donor and non-polychlorinated solvents. The very weakly acidic **34** and **35** were included. The number of aromatic solvents in the basis set is not sufficient to warrant a separate analysis.

$$SPP^N = -95(32) \times 10^{-6}\sigma_{max}$$

$$+0.958(0.060)E_T^N + 2.64(0.70) \tag{18}$$

$$(n = 25, r = 0.974, SD = 0.04)$$

Equation (18) involves all the available data for aliphatic and aromatic (with the exception of **1**) non-hydrogen bond donor solvents. Again, the very weakly acidic **34** and **35** were included.

The contribution of σ_{max} is statistically significant in both cases. At variance with treatments based on equation (13), equations such as (17) and (18) apply to molecules devoid of permanent dipole moments but endowed with large multipoles. This illustrates one of the most appealing features of empirical solvent scales. Furthermore, the present results strongly support previous contentions[21a] regarding the usefulness of linear combinations of π_2^* and π^* (or E_T^N) as tools for correlations of medium effects on reactivity and spectral data. Basically, the present results confirm the fact[13] that, as the a/b ratio in equation (3) can vary within extremely wide limits, no single empirical solvent scale is able to describe all medium effects on reactivity or spectral properties even in the absence of specific interactions unless the ratio a/b takes the same value in the reference scale and in the property under scrutiny. Hence at least two descriptors are generally needed. Therefore, if empirical scales are used, a linear combination of two such scales is required, at least in principle (in practice, data sets seldom contain enough appropriate data to make this need apparent).

Recently, medium effects on the wavenumbers of the carbonyl stretching mode of butanone, $\sigma_{C=O}$ have been reported.[27] The available data are also given in Table 1. They can be analyzed in terms of σ_{max}, E_T^N and π^*_{OMe}. The following equations thus obtain for $\sigma_{C=O}$, and

include all the solvents, with the exception of **18** and **19**:

$$\sigma_{C=O}(cm^{-1}) = 1725.3(0.7) - 15.1(1.2)$$
$$\pi^*_{OMe} (n = 16, r = 0.960, SD = 1.5 \ cm^{-1})$$
(19)

The gas-phase datum is not included in equation (19) but the extrapolated $\sigma_{C=O}$ agrees with the experimental value within less than $2 \ cm^{-1}$.

$$\sigma_{C=O}(cm^{-1}) = 3.7(1.1) \times 10^{-3} \sigma_{max}$$
$$-27.0(2.5)E_T^N + 1642(24)$$
(20)

$$(n = 16, r = 0.955, SD = 1.6 \ cm^{-1})$$

$$\sigma_{C=O}(cm^{-1}) = 2.47(0.92) \times 10^{-3} \sigma_{max}$$
$$-16.5(1.1)\pi^*_{OMe} + 1780(20)$$
(21)

$$(n = 16, r = 0.975, SD = 1.2 \ cm^{-1})$$

Correlation equations (19) and (20) are of essentially the same level of quality, very slightly lower than that of equation (21). Consideration of these data is not sufficient to reach definite conclusions regarding the existence of more 'specific' interactions involving aromatic solvents and the carbonyl group. This situation is unfortunately fairly general as it is extremely difficult to find experimental databases allowing detailed studies of medium effects. The main problem lies in the choice rather than in the number of solvents. Thus, whenever allowed by the nature of the solute and the property under scrutiny, it is important to choose solvents allowing dipolarity and polarizability to vary within the widest possible limits. Inclusion of the gas-phase datum is strongly recommended whenever possible. It is already very clear that solvents devoid of permanent dipole moments but with sizable multipoles are important and must be examined. They should not, however, replace the database of aliphatic and acyclic hydrocarbons. A representative set of aromatic solvents of varying dipolarities is also necessary (benzene is particularly important).

In the cases examined above, the ratio a/b is significant but in some instances this ratio is small. Properties of this kind are prime candidates for correlations with σ_{max} alone. Medium effects on the frequencies of the 0–0 transition of the longest wavelength absorption band in the electronic spectrum of all-*trans*-1,3,5,7-octatetraene,[33] σ_{0-0} (Table 1) are a good example.

Equation (22) holds to a good degree of precision:

$$\sigma_{0-0}(cm^{-1}) = 10.3(2.0) \times 10^3 + 1.025(0.093)\sigma_{max}$$
(22)

$$(n = 7; r = 0.980; SD = 77 \ cm^{-1})$$

This correlation applies to all the available data, including values determined in **13**, **19**, **20** and **50**.

As seen above, σ_{max} is extremely useful for correlation purposes. In this work, however, we have not redefined or otherwise modified the π^*_2 scale before achieving a substantial enlargement of the database.

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