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Solvatochromism of 2-(*N,N*-dimethylamino)-7-nitrofluorene and the natural dye β -carotene: application for the determination of solvent dipolarity and polarizability

Paulo A. R. Pires^a, Muhammad Imran^a, Carina Loffredo^a, Paulo M. Donate^b, Daniel Previdi^b and Omar A. El Seoud^{a*}

The effects of solvents on chemical phenomena (rate and equilibrium constants, spectroscopic transitions, etc.) are conveniently described by solvation free-energy relationships that take into account solvent acidity, basicity and dipolarity/polarizability. The latter can be separated into its components by manipulating the UV-vis spectra of two solvatochromic probes, 2-(*N,N*-dimethylamino)-7-nitrofluorene (DMANF) and a di-(*tert*-butyl)-tetramethyl docosanonaen probe (ttbP9) whose synthesis is laborious and expensive. Recently, we have shown that the natural dye β -carotene can be conveniently employed instead of ttbP9 for the determination of solvent polarizability (SP) of 76 molecular solvents and four ionic liquids. In the present work, we report the polarizabilities of further 24 solvents. Based on the solvatochromism of β -carotene and DMANF, we have calculated solvent dipolarity (SD) for 103 protic and aprotic molecular solvents, and ionic liquids. The dependence of SD and SP on the number of carbon atoms in the acyl- or alkyl group of several homologous series (alcohols; 2-alkoxyethanols; carboxylic acid anhydrides, and esters, ionic liquids) is calculated and briefly discussed. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: solvatochromism; solvent dipolarity; solvent polarizability; 2-(*N,N*-dimethylamino)-7-nitrofluorene; β -carotene; ionic liquids; 2-alkoxyethanols; carboxylic acid esters; acid anhydrides

INTRODUCTION

The effects of solvents on chemical phenomena (rate and equilibrium constants; spectroscopic transitions, etc.) are most conveniently analyzed by solvation free-energy relationships, based on linear combination of solvent parameters, e.g.:

$$\text{Effect of solvent} = a \text{ SA} + b \text{ SB} + d/p \text{ (SD/SP)} \quad (1)$$

Where (S) refers to solvent; (A, B, D/P) refer to solvent "acidity", "basicity" and "dipolarity/polarizability", and (a, b and d/p) are regression coefficients. These represent the susceptibility of the phenomenon in question to the particular solvent property.^[1,2] For consistency, we employ a single, capital letter to refer to a particular solvent property; therefore, (D) and not (dP) stands for solvent dipolarity (SD).

The values of solvent descriptors in Eqn. (1) are most readily calculated by manipulating the UV-vis spectra, absorption or emission, of solvatochromic substances (hereafter designated "probes"), whose spectra are responsive to the properties of the medium. Because these probes are sensitive, to varying extents, to more than one solvent property, the information required is obtained, in general, by manipulating the spectra of pairs of probes, usually homomorphs (molecules that have the same, or closely related molecular structures, e.g. 2-(*N,N*-dimethylamino)-7-nitrofluorene (DMANF) and 2-fluoro-7-nitrofluorene (FNF) for the calculation of (SD/SP), see the molecular structures of some of these probes in Fig. 1.

The last term of Eqn. (1) can be expanded to (d SD + p SP) by using, e.g. the data of DMANF and di-(*tert*-butyl)-tetramethyl

docosanonaen probe (ttbP9), vide infra. This separation of solvent properties is important for the detailed description of phenomena that are sensitive to van der Waals' interactions. There is however, a problem of practical order because obtaining ttbP9 is a major synthetic undertaking, involving an expensive, laborious route, composed of 15 steps!^[3] This difficulty is compounded because the determination of SD for a solvent requires that its SP is known, vide infra. In a recent publication,^[4] we have shown that the natural dye β -carotene, can be conveniently employed for the determination of solvent polarizability (SP); the calculated SP _{β -carotene} were found to be in excellent agreement with SP_{ttbP9} for 68 solvents. We have also reported new SP _{β -carotene} data for 12 solvents, including some ionic liquids, ILs.

We report here SP for additional 26 solvents, as well as new 103 β -carotene-based SD. The solvents investigated included homologous series, e.g. the industrially important 2-alkoxyethanols, ROCH₂CH₂OH, R = C₁ to C₁₀; carboxylic acid anhydrides and their

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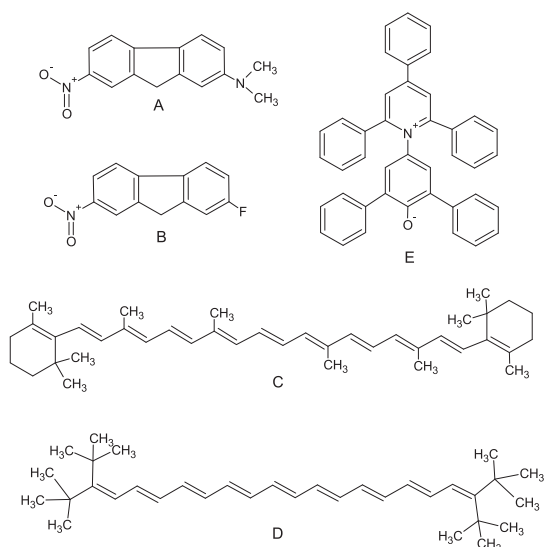


Figure 1. The molecular structures of DMANF (A); FNF (B); (all trans) 1,1'-(3,7,12,16-tetramethyl-1,3,5,7,9,11,13,15,17-octadecanonaen-1,18-diyl) bis [2,6,6-trimethylcyclohexene], β -carotene (C); 3,20-di-tert-butyl-2,2,21,21-tetramethyl-all-trans-3,5,7,9,11,13,15,17,19-docosanonaen, ttbP9 (D), and 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate, RB (E)

ethyl esters; and the ILs 1-R-3-allylimizalolium chlorides, $R = C_6$ to C_{10} . The dependence of SD and SP on the number of carbon atoms in the acyl- or alkyl group of these homologous series is calculated and discussed.

MATERIALS AND METHODS

Chemicals

The chemicals were purchased from Alfa-Aeser or Mensalão Cachoeirense Química; they were purified as given elsewhere,^[5] and stored over activated type 4 Å molecular sieves. Their purity was established by comparing their densities (DMA4500 digital density meter, Anton Paar, Graz) and empirical solvent polarities, $E_T(30)$, with literature values.^[2,6] Values of $E_T(30)$, in kcal mol^{-1} , were calculated from the solvatochromic data of the probe RB, see its molecular structure in Fig. 1. The probe β -carotene (Fluka; $\geq 97\%$) was used as received; its manipulation has been carried out under nitrogen, in absence of direct light. All 2-alkoxyethanols and ILs were available from a previous study.^[4]

The probe DMANF has been synthesized in two steps, as given elsewhere.^[7] First 2,7-dinitrofluorene was reduced into 2-amino-7-nitrofluorene (Pd/C catalyst; formic acid; triethylamine). The latter compound, after purification by flash column chromatography (CH_2Cl_2 eluent; yield 45%), was submitted to reductive amination (reaction with paraformaldehyde) to produce DMANF in 91.0% yield. The m.p. and ^1H NMR spectrum (Varian Innova-300 NMR spectrometer, CDCl_3) were similar to published data.^[7]

UV-vis spectra

UV-vis spectra were recorded with Shimadzu UV-2500 spectrophotometer, under the following conditions: $25 \pm 0.1^\circ\text{C}$ (model 4029 digital thermometer, Control Company, Friendsmood); quartz cells, 1 cm path length; each spectrum was recorded at least thrice, at 140 nm/min; slit width 0.5 nm; sampling interval 0.2 nm. The instrument was routinely checked for λ_{max} accuracy against a holmium oxide glass filter (model 666-F1, Hellma Analytics, Müllheim). The value of (λ_{max}) was determined from the first derivative of the spectrum^[8]; the uncertainty in λ_{max} is ± 0.2 nm.

RESULTS AND DISCUSSION

Separation of SD from SP by using the data of DMANF and β -carotene.

As argued elsewhere, DMANF is sensitive to (SD/SP), whereas ttbP9 is only sensitive to (SP).^[9] We have shown that β -carotene is equivalent to ttbP9 in that it is sensitive only to SP. Therefore, manipulation of the data of DMANF and β -carotene permits calculation of (SD). In what follows, $\tilde{\nu}_{\text{max;probe}}$ refers to the frequency of maximum absorption of a probe in a given solvent. Likewise, SP_{probe} refers to SP, based on β -carotene or ttbP9. The value of $\text{SP}_{\beta\text{-carotene}}$ can be calculated from $\tilde{\nu}_{\text{max;\beta-carotene}}$ by Eqn. (2):

$$\text{SP}_{\beta\text{-carotene}} = \frac{(\tilde{\nu}_{\text{max;\beta-carotene;gas}} - \tilde{\nu}_{\text{max;\beta-carotene;solvent}})}{(\tilde{\nu}_{\text{max;\beta-carotene;gas}} - \tilde{\nu}_{\text{max;\beta-carotene;CS2}})} \quad (2)$$

Where the experimentally unattainable $\tilde{\nu}_{\text{max;probe;gas}}$ (β -carotene is solid) is calculated by extrapolating to zero a plot of $\tilde{\nu}_{\text{max;probe}}$, n -alkanes versus $f(n^2)$ for a homologous series of linear alkanes; $f(n^2)$ is their Lorentz-Lorentz refractive index (n) function; $f(n^2) = (n^2 - 1)/(n^2 + 2)$.

A plot of $\tilde{\nu}_{\text{max;DMANF}}$ against SP ($\text{SP}_{\beta\text{-carotene}}$) is shown in Fig. 2. The data of some solvents (group A = gas phase plus 18 solvents including alkanes, CCl_4 and CS_2 ; SD = 0 in Table 1, vide infra) are located on the straight line, the remaining solvents (group B) clearly deviate from linearity. Whereas the former solvents influence DMANF only through polarizability, group (B) affects $\tilde{\nu}_{\text{max;DMANF}}$ through SD and SP, causing the observed deviations from the straight line. Equation (3) is obtained from the linear regression of group (A) solvents:

$$\begin{aligned} \tilde{\nu}_{\text{max;DMANF,solvent}}^0 &= (28125 \pm 52) - (4861 \pm 79) \text{SP}_{\beta\text{-carotene,solvent}} \quad (3) \\ &(r = -0.9978; \text{sd} = 59.61; N_5 \\ &= 18 \text{ solvents plus gas phase}) \end{aligned}$$

Where the value of $\tilde{\nu}_{\text{max;DMANF}}^0$ represents the maximum frequency that DMANF would have if its interactions with solvent were

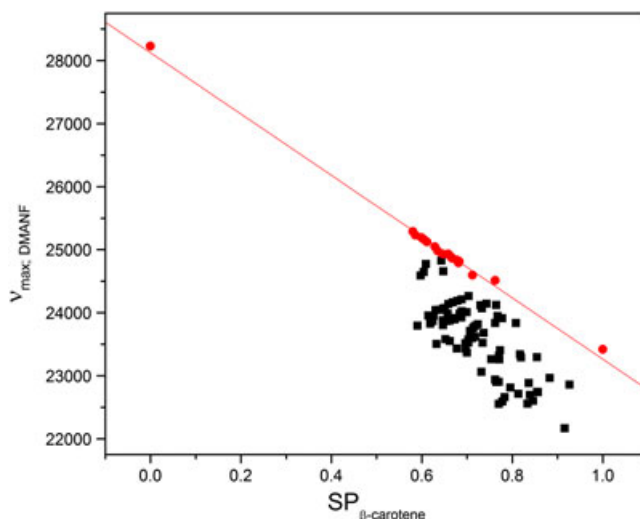


Figure 2. Relationship of $\tilde{\nu}_{\text{max}}$ of DMANF with $\text{SP}_{\beta\text{-carotene}}$ for the solvents studied ($n = 103$) plus gas phase (the largest $\tilde{\nu}_{\text{max;DMANF}}$). The data points on the straight line are those for group (A) solvents

Table 1. Frequencies of the 0-0 component of DMANF, $\tilde{\nu}_{\max, \text{DMANF}}$; the corresponding values of $\tilde{\nu}_{\max, \text{DMANF}}^0$ calculated from Eqn. (3); solvent polarizability ($\text{SP}_{\beta\text{-carotene}}$) and dipolarity ($\text{SD}_{\beta\text{-carotene}}$)

Entry	Solvent	$\tilde{\nu}_{\max} \text{ DMANF, cm}^{-1}, \text{ a,b}$	$\tilde{\nu}_{\max}^0 \text{ DMANF, cm}^{-1}, \text{ c}$	$\text{SP}_{\beta\text{-Carotene}}^{\text{d}}$	$\text{SD}_{\beta\text{-carotene}}^{\text{c}}$
	gas phase	28231	28125	0	0
	Aliphatic and alicyclic hydrocarbon				
1	n-Pentane	25290	25304	0.5803	0
2	3 Methyl pentane	25232	25278	0.5858	0
3	2,2,4 trimethylpentane	25163	25185	0.6048	0
4	n-Hexane	25191	25213	0.5991	0
5	Cyclohexane	24891	24898	0.6639	0
6	Methylcyclohexane	24931	24985	0.6460	0
7	n-Heptane	25125	25153	0.6114	0
8	n-Octane	25047	25067	0.6291 ^c	0
9	n-Nonane	24978	25038	0.6351	0
10	n-Decane	24925	24925	0.6582	0
11	n-Undecane	24934	24925	0.6582 ^c	0
12	n-Dodecane	24863	24883	0.6669	0
13	n- Tetradecane	24839	24835	0.6767	0
14	n-Pentadecane	24792	24814	0.6811	0
15	n-Hexadecane	24814	24805	0.6830	0
16	Decalins (mixture)	24598	24665	0.7119	0
	Halogenated compounds				
17	Dichloromethane	23263	24461	0.7538	0.7906
18	Chloroform	23405	24368	0.7729	0.6403
19	Tetrachloromethane	24513	24420	0.7623	0
20	1,1,1 Trichloroethane	23816	24606	0.7239 ^c	0.5217
21	1,2 Dichloroethane	23258	24376	0.7712	0.7379
22	1-Chlorobutane	23984	24801	0.6838	0.5392
23	chlorobenzene	23288	24143	0.8192	0.5644
24	Fluorobenzene	23681	24544	0.7367	0.5697
25	Hexafluorobenzene	24774	25164	0.6092	0.2572
26	Iodobenzene	22858	23620	0.9267 ^c	0.5030
	Aromatic compounds				
27	Benzene	23913	24344	0.7778	0.2846
28	Toluene	23947	24393	0.7677	0.2945
29	Xylenes (mixture)	24123	24409	0.7644	0.1888
30	Anisole	23339	24152	0.8173	0.5368
31	Tetralin	23890	24196	0.8083	0.2020
32	1-Methylnaphthalene	22966	23833	0.8829	0.5724
	Alcohols				
33	Methanol	23795	25255	0.5904	0.9637
34	Ethanol	23865	25092	0.6239	0.8100
35	1-Propanol	23802	24980	0.6471	0.7773
36	2-Propanol	23825	25117	0.6187	0.8530
37	1-Butanol	23873	24907	0.6620	0.6824
38	2- Butanol	23880	24982	0.6465	0.7276
39	2-Methyl-2-propanol	23955	25137	0.6147	0.7803
40	1-Pentanol	23918	24861	0.6716	0.6221
41	2-Pentanol	23984	24929	0.6574	0.6240
42	1-Hexanol	23923	24782	0.6876	0.5673
43	2-Hexanol	23916	24868	0.6699	0.6287
44	1-Octanol	24009	24725	0.6993	0.4729
45	2-Octanol	24025	24781	0.6879	0.4991
46	Cyclopentanol	23522	24555	0.7345	0.6817
47	Benzyl alcohol	22744	23968	0.8551	0.8081
48	Allyl alcohol	23426	24740	0.6964 ^c	0.8674
49	2-Chloroethanol	22905	24380	0.7704 ^c	0.9736

(Continues)

Table 1. (Continued)

Entry	Solvent	$\tilde{\nu}_{\max}$ DMANF, cm^{-1} , a,b	$\tilde{\nu}_{\max}^0$ DMANF, cm^{-1} , c	$SP_{\beta\text{-Carotene}}^d$	$SD_{\beta\text{-carotene}}^c$
Nitriles					
50	Acetonitrile	23502	25051	0.6324	1.0225
51	Benzonitrile	22693	24045	0.8393 ^c	0.8924
Ethers					
52	1, 2-Dimethoxyethane	23895	24855	0.6727 ^c	0.6338
53	Diethyl ether	24589	25221	0.5975	0.4169
54	Di(2-propyl) ether	24648	25187	0.6043	0.3561
55	Di-(1-butyl) ether	24659	24977	0.6476 ^c	0.2099
56	1,4-Dioxane	24118	24577	0.7298	0.3031
57	THF	23712	24688	0.7070	0.6445
Ketones					
58	Acetone	23580	24954	0.6522	0.9073
59	2-Butanone	23548	24907	0.6620	0.8969
60	Acetophenone	22740	23960	0.8568	0.8055
Carboxylic acid amides					
61	DMF	22939	24421	0.7620	0.9782
62	<i>N,N</i> -dimethylacetamide	22902	24408	0.7647	0.9939
Sulfoxide					
63	DMSO	22557	24072	0.8339	1.000
Pyridine					
64	Pyridine	22883	24060	0.8363	0.7766
Amines					
65	Aniline	22167	23673	0.9158	0.9941
66	<i>N,N</i> -Dimethylaniline	23295	23970	0.8548	0.4453
67	Triethylamine	24824	24997	0.6435	0.1141
Miscellaneous solvents					
68	1,5,9-Cyclododecatriene	23836	24420	0.7623	0.3853
69	Carbon disulfide	23419	23264	1.0000	0
70	Acetic acid	23950	25080	0.6264	0.7460
71	<i>N</i> -Methylimidazole	22558	24013	0.8459	0.9600
72	1-Methyl-2- pyrrolidin-2-one	22711	24171	0.8135	0.9636
Esters					
73	Ethyl acetate	24047	24982	0.6465	0.6174
74	Ethyl propionate	24073 ^c	24961	0.6509 ^c	0.5862
75	ethyl butyrate	24140 ^c	24923	0.6588 ^c	0.5166
76	Ethyl pentanoate	24165 ^c	24876	0.6683 ^c	0.4696
77	Ethyl hexanoate	24187 ^c	24827	0.6784 ^c	0.4227
78	Ethyl decanoate	24209 ^c	24781	0.6879 ^c	0.3776
79	Ethyl dodecanoate	24263 ^c	24704	0.7037 ^c	0.2913
80	Methyl acetate	24044	25060	0.6304 ^c	0.6709
81	1-Propyl acetate	24047	25019	0.6389 ^c	0.6418
82	1-Butyl acetate	24067	24978	0.6473 ^c	0.6015
83	2-propyl acetate	23867 ^c	24944	0.6544 ^c	0.7108
84	Di(1-butyl) phthalate	23316 ^c	24377	0.7710 ^c	0.7005
85	Diethyl carbonate	21999 ^c	24940	0.6552	0.4231
86	Propylene carbonate	23059	24567	0.7320	0.9951
Acid Anhydrides					
87	Acetic Anhydride	23432 ^c	24833	0.6773	0.9246
88	Propionic Anhydride	23515 ^c	24739	0.6966 ^c	0.8077
89	Butanoic Anhydride	23527 ^c	24707	0.7032 ^c	0.7788
90	Pentanoic anhydride	23597 ^c	24670	0.7108 ^c	0.7082
91	Hexanoic anhydride	23618 ^c	24635	0.7179 ^c	0.6716
2-Alkoxyethanols					
92	2-Methoxy ethanol	23368 ^c	24724	0.6996	0.8952
93	2-Ethoxy ethanol	23522 ^c	24714	0.7018	0.7865
94	2-(1-Propyloxy) ethanol	23572 ^c	24707	0.7032	0.7491

(Continues)

Table 1. (Continued)

Entry	Solvent	$\tilde{\nu}_{\max}$ DMANF, cm ⁻¹ , a,b	$\tilde{\nu}_{\max}^0$ DMANF, cm ⁻¹ , c	SP _{β-Carotene} ^d	SD _{β-carotene} ^c
95	2-(1-Butyloxy) ethanol	23635 ^c	24688	0.7070	0.6953
96	2-(1-Pentyloxy) ethanol	23655 ^c	24680	0.7086	0.6769
97	2-(1-Hexyloxy) ethanol	23756 ^c	24655	0.7138	0.5936
98	2-(1-Octyloxy) ethanol	23789 ^c	24637	0.7176	0.5596
99	2-(1-Decyloxy) ethanol	24068 ^c	24563	0.7328	0.3265
Ionic Liquids ^e					
100	AlHxImCl	22552 ^c	24381	0.7702	1.2075
101	AlHplmCl	22589 ^c	24343	0.7781	1.1577
102	AlOclmCl	22658 ^c	24319	0.7830	1.0964
103	AlDclmCl	22813 ^c	24256	0.7960	0.9522

^aFrom Catalán *et al.*^[10,11]
^bFrom Catalán *et al.*^[9]
^cPresent work;
^dFrom Loffredo *et al.*^[4]
^eThe acronyms AlHxImCl, AlHplmCl, AlOclmCl and AlDclmCl refer to 3-allyl-1-alkyl imidazolium chloride, where the alkyl group is 1-hexyl-, 1-heptyl-, 1-octyl- and 1-decyl, respectively.

governed only by SP. Thus, $(\tilde{\nu}_{\max, \text{DMANF, solvent}}^0 - \tilde{\nu}_{\max, \text{DMANF, solvent}})$ represent the dipolarity component of the solvent (i.e. its SD).

For group (B) solvents, the SD value can be obtained from the following equation:

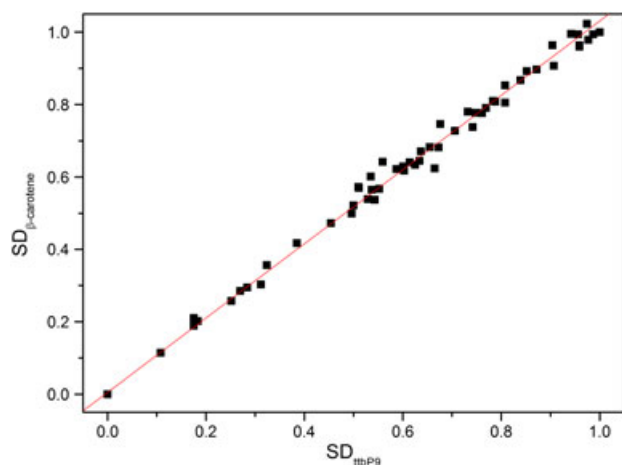
$$SD = \frac{(\tilde{\nu}_{\max, \text{DMANF, solvent}}^0 - \tilde{\nu}_{\max, \text{DMANF, solvent}})}{(\tilde{\nu}_{\max, \text{DMANF, DMSO}}^0 - \tilde{\nu}_{\max, \text{DMANF, DMSO}})} \quad (4)$$

Where the strongly dipolar DMSO is taken as a reference.

In summary, obtaining SD involves the following steps: Calculation of $(\tilde{\nu}_{\max, \text{DMANF, solvent}})$ from the corresponding $(\lambda_{\max, \text{DMANF, solvent}})$ of the charge-transfer band of DMANF in the solvents of interest; determination of the same spectral parameters for β -carotene and calculation of the corresponding SP _{β -carotene} from Eqn. (2); calculation of $\tilde{\nu}_{\max, \text{DMANF, solvent}}^0$ from Eqn. (3); calculation of SD from Eqn. (4). All data are shown in Table 1.

Regarding the data presented in Table 1, the following is relevant:

- (i) – Figure 3 and Eqn. (5) show the correlation between SD _{β -carotene} and SD_{ttbP9} indicating excellent agreement between both scales, with a slope of practically unity. Therefore, the

**Figure 3.** Correlation between SD _{β -carotene} and SD_{ttbP9}

natural dye is a convenient, green and inexpensive substitute for ttbP9.

$$SD_{\beta\text{-carotene}} = (0.005 \pm 0.004) + (1.025 \pm 0.007) \quad (5)$$

$$SD_{\text{ttbP9}} (r = 0.9984; \text{sd} = 0.0203; N_S = 75)$$

- (ii) For each homologous series of compounds, SD _{β -carotene} correlate linearly with the number of carbon atoms, N_c, of the (normal) aliphatic chain present, as shown below:

$$SD_{\beta\text{-carotene, Alcohols}} = 0.9774 - 0.0671 N_c \quad (6)$$

$$(r = 0.9810; \text{sd} = 0.035; N_S = 7)$$

$$SD_{\beta\text{-carotene, 2-Alkoxyethanols}} = 0.9307 - 0.0555 N_c \quad (7)$$

$$(r = 0.975; \text{sd} = 0.042; N_S = 8)$$

$$SD_{\beta\text{-carotene, Esters}} = 0.6497 - 0.0301 N_c \quad (8)$$

$$(r = 0.9649; \text{sd} = 0.033; N_S = 7)$$

$$SD_{\beta\text{-carotene, Anhydrides}} = 1.0109 - 0.0606 N_c \quad (9)$$

$$(r = 0.9520; \text{sd} = 0.03557; N_S = 5)$$

$$SD_{\beta\text{-carotene, Ionic Liquids}} = 1.6037 - 0.0646 N_c \quad (10)$$

$$(r = 0.9968; \text{sd} = 0.01081; N_S = 4)$$

All slopes are negative, i.e. SD decreases as a function of increasing the chain-length of the solvent. The difference in the slopes of alcohols and 2-alkoxyethanols may be traced to the bifunctional nature of the latter. This leads to the formation of several inter- as well as intra-molecular H-bonded species.^[12] The strength of these dipolar functional-group interactions (on the expense of van der Waals interactions) may explain the larger response of the ROH series to N_c, relative to its 2-alkoxyethanol counterpart. The slope for carboxylic anhydride is larger than that of the corresponding esters because the N_c employed refers to a single acyl group. If both groups are considered, however (e.g. N_c = 4 for acetic anhydride), then the slope of both homologous series is practically the same.

(iii) We are reporting SP for new solvents (anhydrides and esters); the corresponding correlations of $SP_{\text{solvent};\beta\text{-carotene}}$ and $f(n)_{\text{solvent}}$ with N_c are listed below:

$$SP_{\text{Esters};\beta\text{-carotene}} = 0.6287 + 0.0089 N_c - 0.0002 (N_c)^2 \quad (r = 0.9704; sd = 0.004; N_s = 7) \quad (11)$$

$$SP_{\text{Anhydrides};\beta\text{-carotene}} = -0.6396 + 0.0229 N_c - 0.0017 (N_c)^2 \quad (r = 0.9812; sd = 0.003; N_s = 5) \quad (12)$$

$$f(n^2)_{\text{Esters}} = 0.2157 + 0.0069 N_c - 0.0003 (N_c)^2 \quad (r = 0.9454; sd = 0.003; N_s = 7) \quad (13)$$

$$f(n^2)_{\text{Anhydride}} = 0.2258 + 0.0062 N_c - 0.0002 (N_c)^2 \quad (r = 0.9811; sd = 0.002; N_s = 5) \quad (14)$$

The slopes of the first-order term are positive, the contribution of the quadratic term is much smaller, i.e. SP increases as a function of increasing N_c , due to enhanced van der Waal's interactions.

CONCLUSIONS

The determination of SD of solvents is made relatively easy because the required SP can be calculated from the solvatochromism of the green, low-cost β -carotene. Based on new values of SP ($N_s = 24$) and $\tilde{\nu}_{\text{max,DMANF}}^0$ ($N_s = 26$), we have reported SD and SP for 103 solvents covering distinct chemical classes. Equation (5) shows that $SD_{\beta\text{-carotene}}$ and SD_{ttbP9} are in excellent

linear correlation with a slope of practically unity. SD and SP are correlated with N_c for homologous series, including both molecular solvents and ILs.

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