

## Convenient Solvatochromic Probes for the Determination of Solvent Properties: $\beta$ -Carotene and 2-Chloro-7-nitro-9H-fluorene

Omar A. El Seoud,\* Paulo A. R. Pires, Carina Loffredo, Muhammad Imran,  
Paolo D. Pulcini, Michelle F. Corrêa and Rizwana Mustafa

Institute of Chemistry, University of São Paulo, CP 26077, 05513-970 São Paulo-SP, Brazil

Dipolaridade/polarizabilidade do solvente (SDP) tem sido calculada a partir dos espectros de UV-Vis de 2-(*N,N*-dimetilamino)-7-nitro-9H-fluoreno e 2-fluoro-7-nitro-9H-fluoreno. Com base em cálculos teóricos (23 solventes) e dados experimentais (56 solventes), revela-se que 2-cloro-7-nitro-9H-fluoreno (disponível comercialmente) pode ser perfeitamente utilizado para o cálculo dessa propriedade, em vez de 2-fluoro-7-nitro-9H-fluoreno. A divisão de SDP nos seus componentes (dipolaridade (SD) e polarizabilidade (SP) do solvente) requer o uso de um composto sintético poliênico cuja síntese é trabalhosa, envolvendo 15 etapas. Nosso grupo de pesquisa mostrou recentemente que o corante natural  $\beta$ -caroteno pode ser convenientemente utilizado para a determinação de SP, permitindo o cálculo de SD. Utilizando estas sondas solvatocromicas, SDP, SP e SD foram calculados para uma série de 1-bromoalcanos. Para várias séries homólogas, a dependência de SDP (SD e SP para uma série homóloga) com o número de átomos de carbono nos grupos 1-alkila ou acila foi calculada e discutida.

Solvent dipolarity/polarizability (SDP) has been previously calculated from the UV-Vis spectra of 2-(*N,N*-dimethylamino)-7-nitro-9H-fluorene and 2-fluoro-7-nitro-9H-fluorene. Based on theoretical calculations (23 solvents) and experimental data (56 solvents), it is shown that 2-chloro-7-nitro-9H-fluorene (commercially available) can be conveniently employed for the calculation of this property, instead of its 2-fluoro-7-nitro counterpart. The splitting of SDP into its components (solvent dipolarity (SD) and polarizability (SP)) requires the use of a synthetic polyene compound whose synthesis is laborious, involving 15 steps. Our research group has recently shown that the natural dye  $\beta$ -carotene can be conveniently employed for the determination of SP, allowing the calculation of SD. Using these solvatochromic probes, SDP, SP and SD for a series of 1-bromoalkanes were calculated. For several homologous series, the dependence of solvent SDP (SD and SP for one series) on the number of carbon atoms in the 1-alkyl- or acyl-group was calculated and discussed.

**Keywords:** solvatochromism, solvent dipolarity/polarizability, solvent dipolarity, solvent polarizability,  $\beta$ -carotene

### Introduction

The effects of solvents on chemical phenomena, e.g., reactivity, equilibrium, spectroscopic transitions, are usually discussed in terms of non-specific and specific interactions between the species of interest (reactants, transition states, etc.) and the solvent. A successful approach to address solvent effects is to use a linear combination of the contributing solvent properties, i.e., a solvation free energy relationship, e.g.:

$$\text{Effect of solvent} = RC_{\text{Acidity}} (\text{solvent acidity}) + RC_{\text{Basicity}} (\text{solvent basicity}) + RC_{\text{Dipolarity/Polarizability}} (\text{solvent dipolarity/polarizability}) \quad (1)$$

where RC stands for regression coefficient. There are several versions of equation 1, e.g., that of Kamlet-Taft-Abboud; equation 2,<sup>1-3</sup> where RCs and the solvent descriptors are termed ( $a$ ;  $b$ ;  $s$ ) and ( $\alpha$ ;  $\beta$ ;  $\pi^*$ ), respectively ( $d\delta$  is a correction term for  $\pi^*$ ); and of Catalán (equation 3),<sup>4</sup> where RCs and the solvent descriptors are termed ( $a$ ;  $b$ ;  $dp$ ) (SA; SB; SDP), respectively. For consistency, the acronym SDP is used instead of SPP employed by Catalán in order to denote solvent dipolarity/polarizability.

\*e-mail: elseoud@iq.usp.br

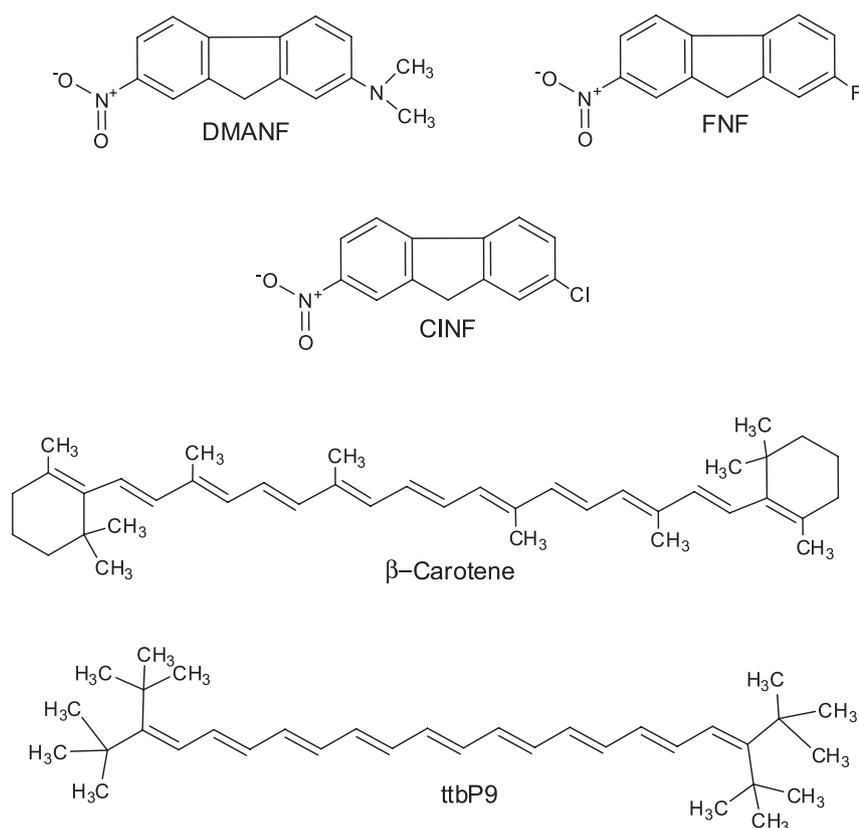
$$\text{Effect of solvent} = a(\alpha) + b(\beta) + s(\pi^* + d\delta) \quad (2)$$

$$\text{Effect of solvent} = a(\text{SA}) + b(\text{SP}) + dp(\text{SDP}) \quad (3)$$

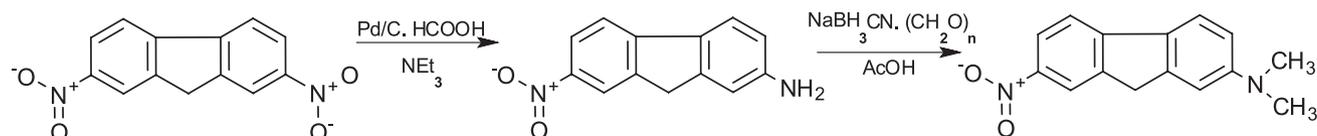
The cavity term has been dropped from equations 1 to 3, because excitation of the probes employed in the present work, *vide infra*, obeys the Franck-Condon principle. Equations 2 and 3 are applied by studying the phenomenon of interest in a series of solvents, followed by correlating the solvent effect with its descriptors (SA, SB, etc.). The relative importance of solvent acidity, basicity, etc. is deduced from the values of the calculated (standardized) regression coefficients. The solvent descriptors on the right-hand side of equations 2 and 3 are called solvatochromic parameters because their values are determined by using solvatochromic substances, hereafter designated as probes. These are dyes whose spectra, absorption or emission, are especially sensitive to solvent properties.<sup>5,6</sup> Figure 1 shows

the molecular structures of the probes of interest to the present work. The pair 2-(*N,N*-dimethylamino)-7-nitro-9*H*-fluorene (DMANF) and 2-fluoro-7-nitro-9*H*-fluorene (FNF) are homomorphs (compounds with closely similar molecular structures) and are employed for the calculation of SDP. As shown elsewhere, the polyene (ttbP9) is sensitive only to solvent polarizability; its use allows splitting of SDP into its components (SD and SP).<sup>4</sup>

The use of some these probes is associated with problems of cost and availability from chemical suppliers. FNF has been discontinued (Aldrich), although custom synthesis is offered; it can be synthesized by nitration of 2-fluoro-9*H*-fluorene.<sup>7</sup> Relative to the commercially available CINF, whose molecular structure is similar to that of FNF, the first choice (custom synthesis) is 10 times more expensive. In addition to the labor involved in the synthesis of FNF from 2-fluoro-9*H*-fluorene, the cost of the latter is twice that of CINF. Therefore, the use of CINF is an attractive alternative



**Figure 1.** Molecular structures of the probes of interest to the present work: 2-(*N,N*-dimethylamino)-7-nitro-9*H*-fluorene (DMANF), 2-fluoro-7-nitro-9*H*-fluorene (FNF), 2-chloro-7-nitro-9*H*-fluorene (CINF), (all *trans*) 1,1'-(3,7,12,16-tetramethyl-1,3,5,7,9,11,13,15,17-octadecanonaene-1,18-diyl) bis[2,6,6-trimethylcyclohexene],  $\beta$ -carotene and 3,20-di-*tert*-butyl-2,2,21,21-tetramethyl-1,3,5,7,9,11,13,15,17,19-docosanoic acid, ttbP9.



**Scheme 1.** Steps of the synthesis of DMANF.

(less cost, no labor) for the determination of SDP, provided that its solvatochromic behavior is similar to that of FNF. The synthesis of ttBP9 is a major synthetic undertaking, involving 15 steps.<sup>8</sup> As recently shown, the natural dye  $\beta$ -carotene can be conveniently employed instead of ttBP9 for the determination of SP.<sup>9</sup>

The aim of the present work is to evaluate the use of CINF instead of FNF for the determination of SDP. Both theoretical calculation (23 solvents) and experimental results (56 solvents) showed excellent linear correlations between the frequencies of maximum absorption of both probes, i.e., CINF is a convenient alternative probe to FNF. The values of SP, hence SD of a series of 1-bromoalkanes, have been determined by using  $\beta$ -carotene and DMANF. The dependence of SDP (also SD and SP of 1-bromoalkanes) on the number of carbon atoms in the alkyl- or acyl chain of the studied liquids was calculated and discussed.

## Experimental

### Materials and synthesis

The chemicals were purchased from Alfa-Aeser or Aldrich; the solvents were purified as shown elsewhere,<sup>10</sup> and stored over activated type 4 Å molecular sieves. The purity of the solvents was established by comparing the values of their densities (DMA-4500 digital density meter, Anton Paar), and overall empirical polarity,  $E_T(30)$  in kcal mol<sup>-1</sup>, with literature ones.<sup>3,11</sup> CINF (99% pure) was employed after drying; its elemental analysis calculated for C<sub>13</sub>H<sub>8</sub>ClNO<sub>2</sub> was found to be (element, %): C, 63.5; H, 3.2; N, 5.7; found: C, 63.4; H, 3.0; N 5.5.

The probe DMANF was synthesized in two steps, as shown in scheme 1.<sup>12</sup> First, 2,7-dinitro-9H-fluorene was partially reduced into 2-amino-7-nitro-9H-fluorene (Pd/C catalyst; formic acid; triethylamine). The latter compound, after purification by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub> eluent; yield 45%), was submitted to reductive amination (reaction with paraformaldehyde) to produce DMANF, 91.0% yield. Elemental analysis calculated for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> was: C, 70.85; H, 5.55; N, 11.02; found: C, 70.56; H, 5.65; N, 10.90. The <sup>1</sup>H nuclear magnetic resonance (NMR) spectral data (Varian Inova-300 NMR spectrometer, CDCl<sub>3</sub>) were similar to those published elsewhere.<sup>12</sup>

### UV-Vis absorption spectra

UV-Vis spectroscopic measurements were carried out on a Shimadzu UV-2500 spectrophotometer, equipped with a model 4029 digital thermometer (Control Company),

under the following experimental conditions: each spectrum was recorded at least thrice, at 140 nm min<sup>-1</sup>; slit width 0.5 nm; sampling interval of 0.2 nm. The instrument was routinely checked for  $\lambda_{\max}$  accuracy against the known peaks of a holmium oxide glass filter (model 666-F1, Hellma Analytics, Müllheim). Maximum wavelength was determined from the first derivative function, calculated by using a commercial software (GRAMS/32 version 5.10, Galactic Industries); the uncertainty in  $\lambda_{\max}$  is  $\pm 0.2$  nm. All spectra were recorded at  $25 \pm 0.1$  °C using quartz cells of 1 cm path length.

### Calculations

#### Solvent SDP, SP and SD<sup>4,9</sup>

The value of SDP is calculated from equation 4:

$$\text{SDP} = \frac{\Delta\tilde{\nu}_{\max;\text{probe};\text{solvent}} - \Delta\tilde{\nu}_{\max;\text{probe};\text{gas}}}{\Delta\tilde{\nu}_{\max;\text{probe};\text{DMSO}} - \Delta\tilde{\nu}_{\max;\text{probe};\text{gas}}} \quad (4)$$

where  $\Delta\tilde{\nu}_{\max;\text{probe};\text{solvent}}$  is the difference between the wavenumbers of the longest wavelength (i.e., the solvatochromic) transition of the probes CINF and DMANF in the solvent of interest i.e.,  $(\tilde{\nu}_{\text{CINF};\text{solvent}} - \tilde{\nu}_{\text{DMANF};\text{solvent}})$ ;  $\Delta\tilde{\nu}_{\max;\text{probe};\text{gas}}$  is the same difference, but in the gas phase; and  $\Delta\tilde{\nu}_{\max;\text{probe};\text{DMSO}}$  is the corresponding value for (the reference solvent) DMSO.

The experimentally unattainable  $\tilde{\nu}_{\max;\text{probe};\text{gas}}$  (all indicators are solid) is calculated by extrapolation to zero a plot of  $\tilde{\nu}_{\max;\text{probe};\text{n-alkanes}}$  vs. the Lorenz-Lorentz refractive index function  $f(n)^2 = (n^2 - 1)/(n^2 + 2)$  (where  $n$  = refractive index) for a homologous series of linear alkanes. The values of  $\tilde{\nu}_{\max;\text{probe};\text{gas}}$  are listed at the top of Table S1 in the Supplementary Information (SI) section; the corresponding one for  $\beta$ -carotene is 24402 cm<sup>-1</sup>.<sup>9</sup>

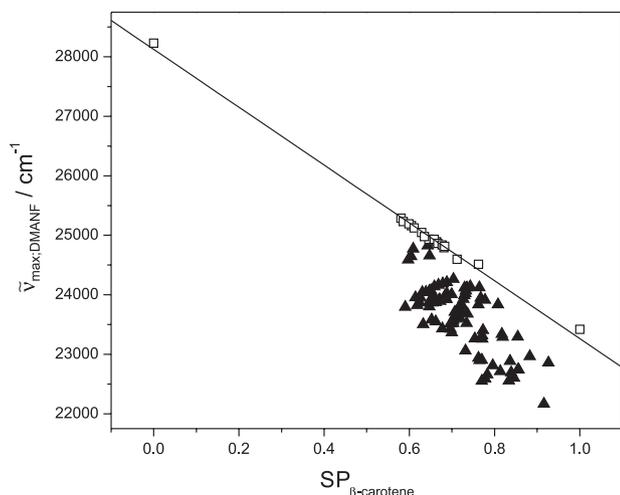
Manipulation of the data of DMANF and  $\beta$ -carotene permits the calculation of SD, as shown by equation 5:

$$\text{SP}_{\beta\text{-carotene}} = \frac{\tilde{\nu}_{\max;\beta\text{-carotene};\text{gas}} - \tilde{\nu}_{\max;\beta\text{-carotene};\text{solvent}}}{\tilde{\nu}_{\max;\beta\text{-carotene};\text{gas phase}} - \tilde{\nu}_{\max;\beta\text{-carotene};\text{CS}_2}} \quad (5)$$

The plot of  $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}$  vs.  $\text{SP}_{\beta\text{-carotene};\text{solvent}}$  is shown in Figure 2, in which the solvents can be grouped into two classes. Group A is located on a straight line; the rest (group B) clearly deviates from linearity. Group A includes gas phase plus alkanes, CCl<sub>4</sub> and CS<sub>2</sub>. These are solvents that influence DMANF only through their polarizability. Group B solvents affect  $\tilde{\nu}_{\max;\text{DMANF}}$  through SD and SP, this leads to deviations from the straight line. Equation 6 is obtained from the linear regression of the straight line of Figure 2:

$$\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}^{\circ} = (28134 \pm 49) - (4884 \pm 75) \text{SP}_{\beta\text{-carotene};\text{solvent}} \quad (\text{NS} = 18; \text{sd} = 56.373; r = -0.9981) \quad (6)$$

where the value  $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}^{\circ}$  represents the frequency that DMANF would have if its interaction with the solvents were governed only by SP. Thus, the difference between  $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}^{\circ}$  and  $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}$  is proportional to the dipolarity component of this solvent, i.e., its SD.



**Figure 2.** Correlation between  $\tilde{\nu}_{\max;\text{DMANF}}$  and  $\text{SP}_{\beta\text{-carotene}}$  for different media: group A (squares, including gas phase) and group B (triangles).

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

$$\text{SD} = \frac{\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}^{\circ} - \tilde{\nu}_{\max;\text{DMANF};\text{solvent}}}{\tilde{\nu}_{\max;\text{DMANF};\text{DMSO}}^{\circ} - \tilde{\nu}_{\max;\text{DMANF};\text{DMSO}}} \quad (7)$$

where the strongly dipolar DMSO is taken as a reference.

Therefore, the calculation of SD involves the following steps: determination of  $(\lambda_{\max;\text{DMANF};\text{solvent}})$  of the DMANF charge-transfer band in the solvents of interest, and subsequent calculation of the corresponding frequency ( $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}$ ); determination of the same spectral parameters for  $\beta$ -carotene and calculation of the corresponding  $\text{SP}_{\beta\text{-carotene}}$  from equation 5; calculation of  $\tilde{\nu}_{\max;\text{DMANF};\text{solvent}}^{\circ}$  from equation 6; and calculation of SD by application of equation 7.

#### Geometry optimization of the structures of FNF and CINF

FNF and CINF had their geometries, in the gas phase, optimized in two steps, both using a density functional theory (DFT) calculation that employs B3LYP density functional; 6-311G(d,p) and CC-pVDZ basis sets were employed.

For both probes, the transition energies between the fundamental and excited state were calculated by time-

dependent density functional theory (TD-DFT), using BOP density functional and DH (Dunning/Hay double zeta) basis set with the application of long range correction. Values of frequencies of maximum absorption ( $\tilde{\nu}_{\max}$ ) of the excited states with the largest oscillator strength are shown in Table S2 in the SI section. Solvent effects were simulated by using the polarizable continuum model (PCM) combined with SMD solvation model. The solvation free energy ( $\Delta G_{\text{solvation}}$ ) was calculated from the difference between the free energy of the probe (ground state) in the solvent and in the gas phase. All calculations were performed by using the version Oct 1 2010 (R3) of Gamess US program package.<sup>13</sup>

The quality of geometry optimization of both probes can be shown by the agreement between calculated bond lengths and angles with X-ray data of fluorene (to our knowledge, there are no X-ray data for FNF, CINF or 7-nitro-9H-fluorene), see Table S3 in the SI section.

## Results and Discussion

Can CINF be reliably employed instead of FNF for the determination of SDP?

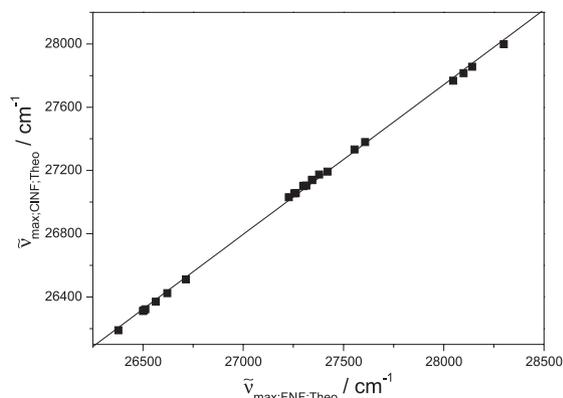
In order to answer this question, two strategies were employed: (i) theoretically calculated energies of solvation and the  $\tilde{\nu}_{\max}$  of both CINF and FNF for a set of representative solvents were compared; (ii) the experimental  $\tilde{\nu}_{\max}$  values for a large set of solvents were compared.

#### Theoretical calculations

With regard to (i), the following procedure was employed for each probe: the geometry was optimized in the gas phase; the optimized probes were then solvated in solvents for which parameterized data are available in the employed software package, *vide supra*. The set chosen covers nonpolar and weakly polar aliphatic and aromatic hydrocarbons, dipolar aprotic solvents, and aliphatic alcohols.  $\Delta G_{\text{solvation}}$  and the values of  $\tilde{\nu}_{\max}$  for both probes were calculated; the results are listed in Table S2 in the SI section.

Equations 8 and 9 (NS = number of solvents investigated; sd = standard deviation; r = correlation coefficient) and Figure 3 clearly show that there are excellent correlations between  $\Delta G_{\text{solvation}}$  and  $\tilde{\nu}_{\max;\text{Theo}}$  for both probes in the different solvents, with slopes of practically, or not far from unity. This indicates that the energies of solvation of the two probes are very similar; hence their solvatochromism responses to the same set of solvents correlate linearly.

$$\Delta G_{\text{Solvation};\text{CINF};\text{Theo}} = -0.839 + 1.003 \Delta G_{\text{Solvation};\text{FNF};\text{Theo}} \quad (\text{NS} = 23; \text{sd} = 0.0831; r = 0.9989) \quad (8)$$

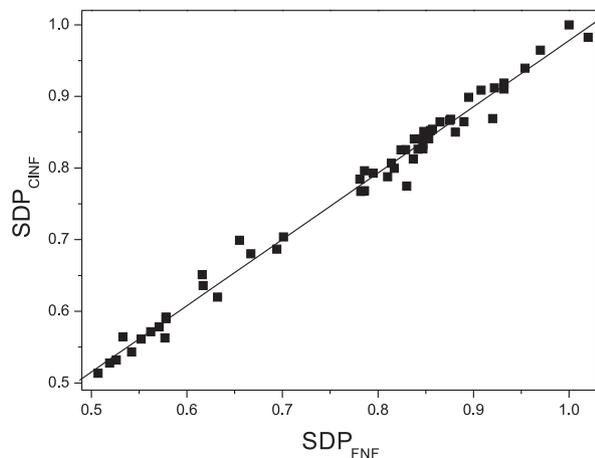


**Figure 3.** Correlation between theoretically calculated frequencies of maximum absorption,  $\tilde{\nu}_{\max;\text{probe}}$  of FNF and CINF.

$$\tilde{\nu}_{\max;\text{CINF;Theo}} = 1237 + 0.947 \tilde{\nu}_{\max;\text{FNF;Theo}} \quad (\text{NS} = 23; \text{sd} = 17.634; r = 0.9995) \quad (9)$$

Comparison of the experimental  $\tilde{\nu}_{\max;\text{Exp}}$  and the calculated SDP values

The experimental values of  $\tilde{\nu}_{\max;\text{FNF;Exp}}$ ,  $\tilde{\nu}_{\max;\text{CINF;Exp}}$  and  $\tilde{\nu}_{\max;\text{DMANF;Exp}}$  are listed in Table S1 in the SI section, along with the corresponding SDP. The equations employed for the calculations of these parameters are given in the Calculations item in the Experimental section.



**Figure 4.** Correlation between experimental SDP values of FNF and CINF.

The excellent agreement between the solvatochromic responses of CINF and FNF is evident from equations 10 and 11 and in Figure 4 (for representative solvents).

$$\tilde{\nu}_{\max;\text{CINF;Exp}} = (2671 \pm 268) + (0.910 \pm 0.001) \tilde{\nu}_{\max;\text{FNF;Exp}} \quad (\text{NS} = 56; \text{sd} = 29,395; r = 0.9948) \quad (10)$$

$$\text{SDP}_{\text{CINF;Exp}} = (0.05 \pm 0.01) + (0.93 \pm 0.01) \text{SDP}_{\text{FNF;Exp}} \quad (\text{NS} = 56; \text{sd} = 0.0149; r = 0.9872) \quad (11)$$

Both results show that our initial expectation is confirmed, i.e., because of the similar molecular structures, both probes respond similarly to solvent dipolarity/polarizability, 2-chloro-7-nitro-9*H*-fluorene (CINF) is a convenient probe for the determination of SDP.

After establishing that CINF can be employed instead of FNF, SDP was determined for a series of 1-bromoalkanes that are extensively employed in the synthesis of ionic liquids with increasing hydrophobic character.<sup>14</sup> DMANF and  $\beta$ -carotene were employed as solvatochromic probes in order to determine SD and SP for these liquids, the results are listed in Table 1.

**Table 1.** Values of SP and SD for homologue series of 1-bromoalkanes<sup>a</sup>

entry	Compound	$\tilde{\nu}_{\max, \beta\text{-carotene}} / \text{cm}^{-1}$	SD	SP
1	1-bromoethane	21750	0.593	0.722
2	1-bromobutane	21741	0.525	0.725
3	1-bromohexane	21734	0.438	0.727
4	1-bromooctane	21724	0.390	0.729
5	1-bromodecane	21715	0.360	0.732
6	1-bromododecane	21703	0.286	0.735

<sup>a</sup>The equations employed for the calculations of these parameters are given in the Calculations item of the Experimental section.

The dependence of SDP of some homologous series (Table S1 in SI) on the number of carbon atoms ( $N_c$ ) in the alkyl- or acyl group of the compounds are shown below, along with the same dependence of SD and SP for 1-bromoalkanes:

(i) Bromoalkanes:

$$\text{SDP} = 0.914 - 0.057 N_c - 0.005 N_c^2 \quad (\text{NS} = 6, \text{sd} = 0.017; r = 0.9685) \quad (12)$$

$$\text{SD} = 0.643 - 0.035 N_c \quad (\text{NS} = 6, \text{sd} = 0.015, r = 0.9932) \quad (13)$$

$$\text{SP} = 0.718 + 0.001 N_c \quad (\text{NS} = 6, \text{sd} = 0.001, r = 0.9784) \quad (14)$$

(ii) Linear-chain alcohols:

$$\text{SDP} = 0.866 - 0.013 N_c \quad (\text{NS} = 7, \text{sd} = 0.003, r = 0.9954) \quad (15)$$

(iii) 2-Alkoxyethanols:

$$\text{SDP} = 0.903 - 0.015 N_c \quad (\text{NS} = 9, \text{sd} = 0.006, r = 0.9959) \quad (16)$$

(iv) Ethyl esters of carboxylic acids:

$$\text{SDP} = 0.802 - 0.010 N_c \quad (\text{NS} = 7, \text{sd} = 0.009, r = 0.9779) \quad (17)$$

(v) Ionic liquids:

$$\text{SDP} = 0.999 - 0.019 N_c \quad (\text{NS} = 6, \text{sd} = 0.007, r = 0.9946) \quad (18)$$

Except for one case (1-bromoalkanes), the dependence of SDP on  $N_c$  is linear; for these (linear) plots, the slopes are negative, i.e., the dipolarity/polarizability decreases as a function of increasing chain length of the compound. The reason for the non-linear dependence of SDP on  $N_c$  for 1-bromoalkanes is not readily explainable at present; data for several homologous series should be examined. It is relevant however, that the slopes of the SD and SP vs.  $N_c$  plots for this series are negative and positive, respectively. This behavior agrees with chemistry because dipolar interactions are expected to decrease as a function of increasing alkyl-chain length while keeping the dipolar bond ( $-\text{C}^{\delta+}-\text{Br}^{\delta-}$ ) constant. On the other hand, the Lorenz-Lorentz refractive index function of this series (a measure of SP) increases as a function of increasing  $N_c$ .

## Conclusions

The results of theoretical calculations and experimental data clearly lead to the same conclusion: CINF and FNF respond similarly to solvent dipolarity/polarizability. This similarity, as evidenced by equations 10 and 11, and Figures 3 and 4, argues convincingly that both probes can be employed interchangeably for the calculation of SDP. The commercial availability of CINF and the green dye  $\beta$ -carotene at reasonable cost simplify the determination of the solvatochromic parameters, a prerequisite for understanding the effects of solvents on chemical phenomena. For homologous series, the dependence of SDP, SD and SP on their molecular structures is mostly linear, showing that the effects of increasing chain length of the alkyl- or acyl group on these solvent properties are additive.

## Supplementary Information

Supplementary Information of this article is available free of charge at <http://jbcs.sbc.org.br> as a pdf file.

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