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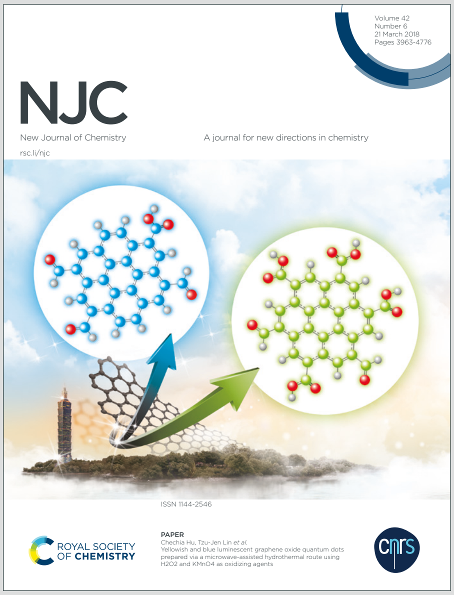

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Understanding the efficiency of ionic liquids-DMSO as solvents for carbohydrates: Use of solvatochromic- and related physicochemical properties

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Abstract

The physical dissolution of carbohydrates (cellulose, chitin, and starch), i.e., without formation of covalent bonds requires that the solvent possess certain physicochemical properties. Concentrating on cellulose, the solvent should act both as Lewis acid, and Lewis base, and disrupt the present hydrophobic interactions, as the biopolymer has amphiphilic character. Quantification of the relative importance of these physicochemical properties helps in predicting solvent structures expected to be efficient as cellulose solvents. Ionic liquids (ILs) are extensively used as carbohydrate solvents because they disrupt intramolecular-, intermolecular-, and hydrophobic interactions within the biopolymer structure, leading to its dissolution. Solvatochromic substances (probes) are especially sensitive to one, or more of the above-mentioned biopolymer-solvent interactions. Consequently, they are used to predict, and rationalize solvent efficiency. The solvent parameters (descriptors) most widely employed are: empirical polarity, E_T(probe), Lewis acidity (*SA*); Lewis basicity (*SB*), dipolarity (*SD*), and polarizability (*SP*); S refers to solvent. We synthesized 18 ILs, including derivatives of imidazole, 1,8-diazabicyclo[5.4.0]undec-7-ene, and tetramethylguanidine; the corresponding anions are carboxylates, chloride and dimethylphosphate. We used solvatochromic probes to calculate the descriptors of IL-DMSO (at fixed DMSO mole fraction of 0.6; 40 °C), and correlated E_T(probe) with the other descriptors. We also tested the correlations by using the molar volume of the IL (V_M) instead of SD, and Lorentz-Lorenz refractive index function $f(n)$ of the IL-DMSO mixture instead of SP. The quality of the regression analysis increased noticeably when we limited the ILs correlated to those based on imidazole (13 ILs), and used (V_M) and

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ƒ(n). The regression coefficients showed that *SA* is the most important descriptor; solvent empirical polarity is inversely dependent on V_M. The value of *ƒ(n)* shows the importance of hydrophobic interactions. By using different probes, we showed that the observed small contribution of *SB* reflects steric crowing around the positive nitrogen atom in some probes. The results obtained help in selecting ILs as solvents for cellulose and other carbohydrates, based on the expected strength of their interactions with the biopolymers. Therefore, using solvatochromism for solvent efficiency screening saves labor and cost.

Key Words

Solvatochromism, solvatochromic descriptors, ionic liquids, cellulose dissolution, correlation of solvent descriptors, biopolymer-solvent interactions.

1- Introduction

Several solvents and their mixtures dissolve carbohydrate polymers, e.g., cellulose, chitin and starch physically, i.e., without covalent bond formation.[1-9] The resulting solutions are used to regenerate the biopolymer, e.g., as fibers, films, and nanoparticles, and to synthesize derivatives, e.g., esters and mixed esters.[10-14] Considering cellulose, derivatization under homogeneous reaction conditions leads to products with better control of regioselectivity and degree of substitution both in the biopolymer structural unit (anhydroglucose unit; AGU), and along its backbone. Consequently, the products thus obtained show reproducible properties, e.g., dissolution in solvents and their mixtures.[14,15] As cotton production is not expected to meet world demand for fabrics,[16] the use of cellulose from other sources, in particular wood is expected to expand. Use of the latter involves biopolymer dissolution followed by fiber regeneration in a suitable bath. Consequently, there is intense and sustained interest in the physical dissolution of cellulose.[17]

For the above-mentioned biopolymers there is interest is understanding the following aspects: (i) the mechanism of their physical dissolution; (ii) assessment of the solvent physicochemical properties that lead to efficient biopolymer dissolution. As both issues were studied in much more details for cellulose, we focus on the dissolution of this biopolymer, although the conclusions apply to other biopolymers, at

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least qualitatively. Regarding (i), there is agreement that the solvent should disrupt the inter- and intramolecular hydrogen-bonding (H-bonding) present, as well as the hydrophobic interactions because cellulose has amphiphilic character.[18,19] This raises the following question: Is it possible to quantify the relative importance to cellulose dissolution of H-bonding and hydrophobic interactions? In the present work we discuss a strategy to answer this question with emphasis on the use of solvatochromic parameters (*vide infra* the definition of solvatochromism) and other, alternative physicochemical properties of the solvent.

We synthesized 18 ionic liquids (ILs) that are known (based on literature) to dissolve cellulose.[4,5,9,14,20-23] These include derivatives of imidazole; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and tetramethylguanidine (TMG). Of these, fifteen IL have carboxylate anions, and three have chloride and dimethylphosphate anions.[24] It is known that binary mixtures of ILs and molecular solvents (MSs) are, in many cases, more efficient as cellulose solvents than pure ILs.[18,25] Consequently, we used these ILs as solutions in dimethyl sulfoxide (DMSO), at a fixed mole fraction of the MS; $\chi_{\mathbf{DMSO}} = 0.6$. We employed this binary solvent composition because our previous data on cellulose dissolution in mixtures of several ILs and DMSO showed biopolymer dissolution maxima at $\chi_{\mathbf{DMSO}}$ of ca. 0.6.[23] We calculated the solvatochromic parameters of these binary mixtures (BMs), and correlated them. We also examined the use of other physicochemical properties of the solvent, namely IL molar volume (V_M) and the Lorentz-Lorenz refractive index function $f(n)$ of the BM. Our data showed that limiting the molecular structure of the ILs to imidazole derivatives (13 ILs) resulted in satisfactory multi-parameter correlation whose quality was further enhanced by including (V_M) and f(n) instead of (solvatochromic-based) solvent dipolarity and polarizability, respectively. The most relevant solvent parameters that contribute to its empirical (or total) polarity, hence to biopolymer dissolution, are those related to H-bonding.

2-Experimental

We purchased all reagents and solvents from Sigma-Aldrich or Synth (São Paulo) and purified them as given elsewhere.[26]

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2.1- Synthesis of the ionic liquids

Table 1 shows the molecular structures of the synthesized ILs and their physicochemical parameters of interest. We discuss later the calculation of these parameters. We list the ^{1}H NMR data (Varian Innova-300, 300 MHz for ^{1}H, $CDCl_3$) for all ILs synthesized in **Table ESI-1** (Table 1 of Electronic Supplementary Information).

Table 1: Molecular structures of the ionic liquids (ILs) employed; physicochemical properties of the binary mixtures IL-DMSO, at $\chi_{\mathbf{DMSO}}$ = 0.6, and 40°C, and molecular volumes of the pure ILs.[a]

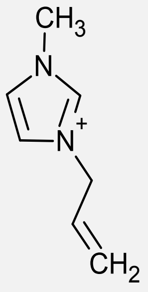
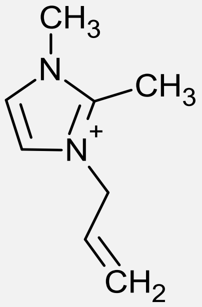
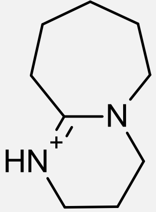
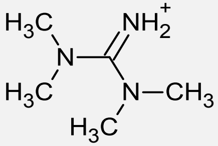
Cation	**Anion**	**E_T(WB); kcal/mol**	***SA***	***SB***	***SD***	***SP***	**V_M; cm^3/mol**	**n**	***f(n)***
 **$AlMeIm^+$**	Acetate	57.72	0.156	0.928	1.169	0.865	183.03	1.4988	0.2959
	Benzoate	56.97	0.157	0.791	0.808	0.919	237.88	1.5189	0.3024
	Chloride	58.39	0.170	0.716	0.982	0.843	153.82	1.4990	0.2932
	Formate	57.70	0.158	0.738	1.196	0.876	166.47	1.5045	0.2972
	2-Methoxyacetate	57.40	0.159	0.720	1.019	0.863	208.82	1.5030	0.2956
	Propionate	57.04	0.155	0.935	0.927	0.871	199.84	1.5023	0.2966
 **$AlMe_2Im^+$**	Acetate	56.08	0.135	0.958	1.211	0.873	199.59	1.5057	0.2968
	Benzoate	55.24	0.136	0.799	1.253	0.937	254.44	1.5248	0.3046
	Chloride	56.40	0.151	0.731	1.116	0.848	170.38	1.5031	0.2938
	Dimethylphosphate	55.70	0.147	0.764	1.219	0.831	243.49	1.4938	0.2917
	Formate	56.78	0.149	0.742	1.097	0.86	183.03	1.5022	0.2952
	2-Methoxyacetate	56.25	0.150	0.744	1.109	0.864	225.38	1.5033	0.2957
	Propionate	55.73	0.134	0.965	1.042	0.882	216.40	1.5074	0.2979

Table 1, continue.

Cation	**Anion**	***E_T*(WB); kcal/mol**	***SA***	***SB***	***SD***	***SP***	***V_M*; cm³/mol**	**n**	***f(n)***
 **DBUH⁺**	Acetate	58.91	0.051	0.891	1.149	0.824	217.71	1.4961	0.2909
	Formate	58.27	0.052	0.828	1.123	0.823	201.15	1.4974	0.2907
	2-Methoxyacetate	58.07	0.054	0.873	1.026	0.834	243.50	1.4952	0.2921
	Propionate	58.33	0.048	0.905	1.007	0.896	239.24	1.5070	0.2996
 **TMGH⁺**	Acetate	57.96	0.164	0.816	1.022	0.802	182.82	1.4862	0.2872

a- The solvent parameters listed for the IL-DMSO mixtures ($\chi_{\mathrm{DMSO}} = 0.6$) are: empirical polarity (*E_T*(WB)), Lewis acidity (*SA*), Lewis basicity (*SB*), dipolarity (*SD*), polarizability (*SP*), refractive index (n) and Lorentz-Lorenz refractive index function *f(n)*. The molar volume (*V_M*) is that of the pure IL.

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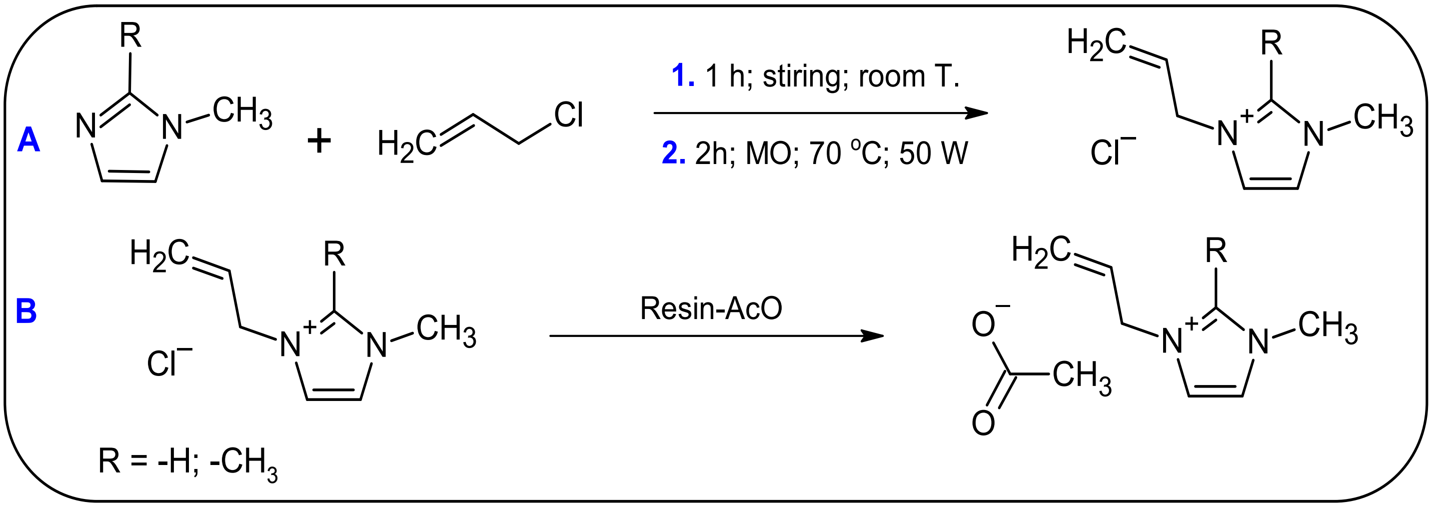
2.1.1- Synthesis of ionic liquids based on 1-methyl- and 1,2-dimethylimidazole.

We synthesized these ILs according to the general **scheme-1**; the example we show is that of 1-allyl-3-methylimidazolium acetate (AlMeImAcO). The steps included: preparation of the IL in chloride form (1-allyl-3-methylimidazolium chloride; AlMeImCl); transformation of ion-exchange macroporous resin into acetate (resin-OH → resin-AcO);[21] conversion of (AlMeImCl → AlMeImAcO).



Scheme-1: Synthesis of 1-methyl- and 1,2-dimethylimidazole-based ILs, via alkylation (A) followed by ion exchange (B).

We synthesized AlMeImCl by microwave (CEM-Discover DU-8316) assisted reaction of 1-methylimidazole with allyl chloride in acetonitrile (MeCN). A solution of allyl chloride (40.7 mL; 0.5 mol) in 20 mL MeCN was added slowly (1 h) to a solution of 1-methylimidazole (42 mL; 0.5 mol) in 50 mL MeCN at room temperature. We heated the reaction mixture at 70 °C for 2h (50 W irradiation power) and then removed MeCN. We purified the produced AlMeImCl by vigorous agitation with hot ethyl acetate (3 x 40 mL each; 10 minutes), followed by phase separation at room temperature (IL is the lower phase), and removal of residual ethyl acetate under reduced pressure. Yield= 90%.

We converted the above-mentioned IL into the corresponding acetate using Amberlite IRN-78, 1.2 mmol OH/mL resin. First, the resin was converted into the acetate form by agitation with an aqueous solution of acetic acid (5 mol % excess acid) for 2 h. We filtered the resin, and

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suspended it in water several times to remove the excess acid (vigorous agitation, 10 minutes each), and then conditioned the resin in methanol. We dissolved 31.73g AlMeImCl (0.2 mol) in 500 mL methanol and passed the solution *slowly* through a column containing 250 mL of Res-AcO, followed by 250 mL of methanol. We checked the completeness of ion exchange by adding aliquots of the eluted solution to $AgNO_3/HNO_3$ solution; no precipitate was formed. We removed methanol, and then dried the obtained IL under reduced pressure, over P_4O_{10} until constant mass; yield 95%. The other IL-carboxylates were obtained by a similar protocol, i.e., using Resin-PrO, etc. All ILs are slightly yellowish viscous liquids or soft pastes; they gave satisfactory ^{1}H NMR data; *vide* **Table ESI-1**.

2.1.2- Synthesis of ionic liquids based on DBU and TMG.

We synthesized these ILs as given elsewhere[22,27] by carefully neutralized a solution of the super-base (0.2 mol/25 mL MeCN) with the appropriate carboxylic acid (0.2 mol/25 mL MeCN), under nitrogen at 0 ^oC, followed by agitation for 1h at room temperature. We removed MeCN and dried the IL under reduced pressure, over P_4O_{10} until constant mass; yields 87 to 93%. The DBU-based ILs are pale-yellow liquids; TMG-based IL is a white solid.

*2.1.3- Synthesis of 1-allyl-2,3-dimethylimidazolium dimethylphosphate (**$AlMe_2ImMe_2P$**)*

We synthesized this IL according to **scheme-2** below.[24] The product is a pale-yellow liquid that gave satisfactory ^{1}H NMR spectrum, see **Table ESI-1**. We obtained 1-allyl-2-methylimidazole in 55 % yield and $AlMe_2ImMe_2P$ in 80% yield.

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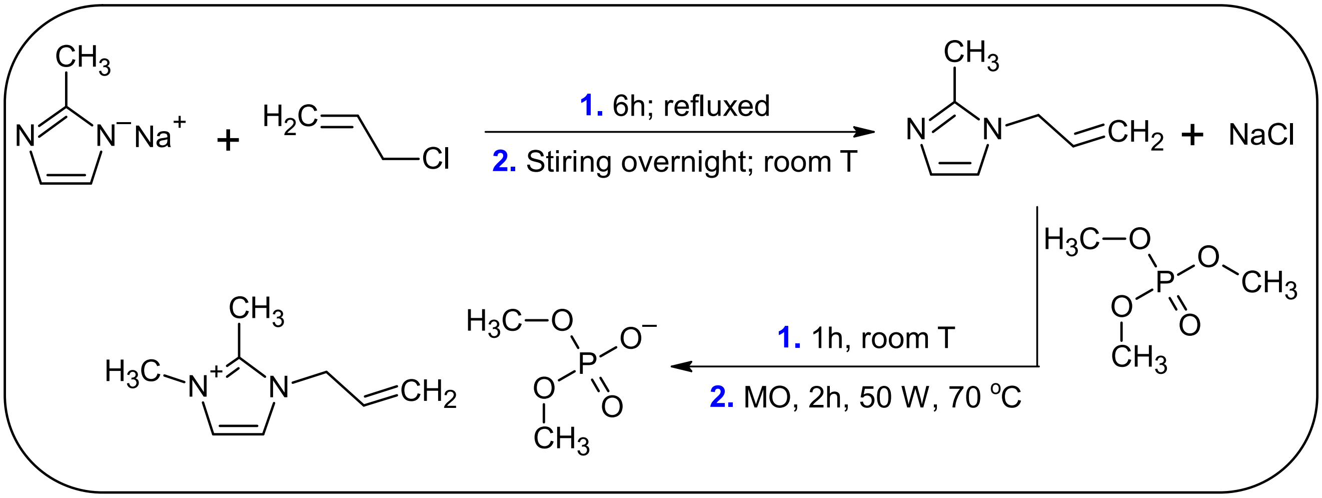

Scheme 2: Synthesis of 1-allyl-2,3-dimethylimidazole dimethylphosphate from 1-allyl-2-methylimidazole followed by its alkylation by trimethylphosphate.

2.2- Solvatochromic indicators (probes)

We show in **Figure 1** the solvatochromic indicators employed in the present work, along with other probes that we will discuss. We attach to each probe (or pairs of probes) the solvent descriptor that it is used to calculate. These are referred to as (where S is the solvent): empirical polarity (E_T(RB), E_T(WB)), E_T(MePMeBr$_2$); solvent Lewis acidity, *SA*; solvent Lewis basicity, *SB*; solvent dipolariy, *SD*; solvent polarizability, *SP*.

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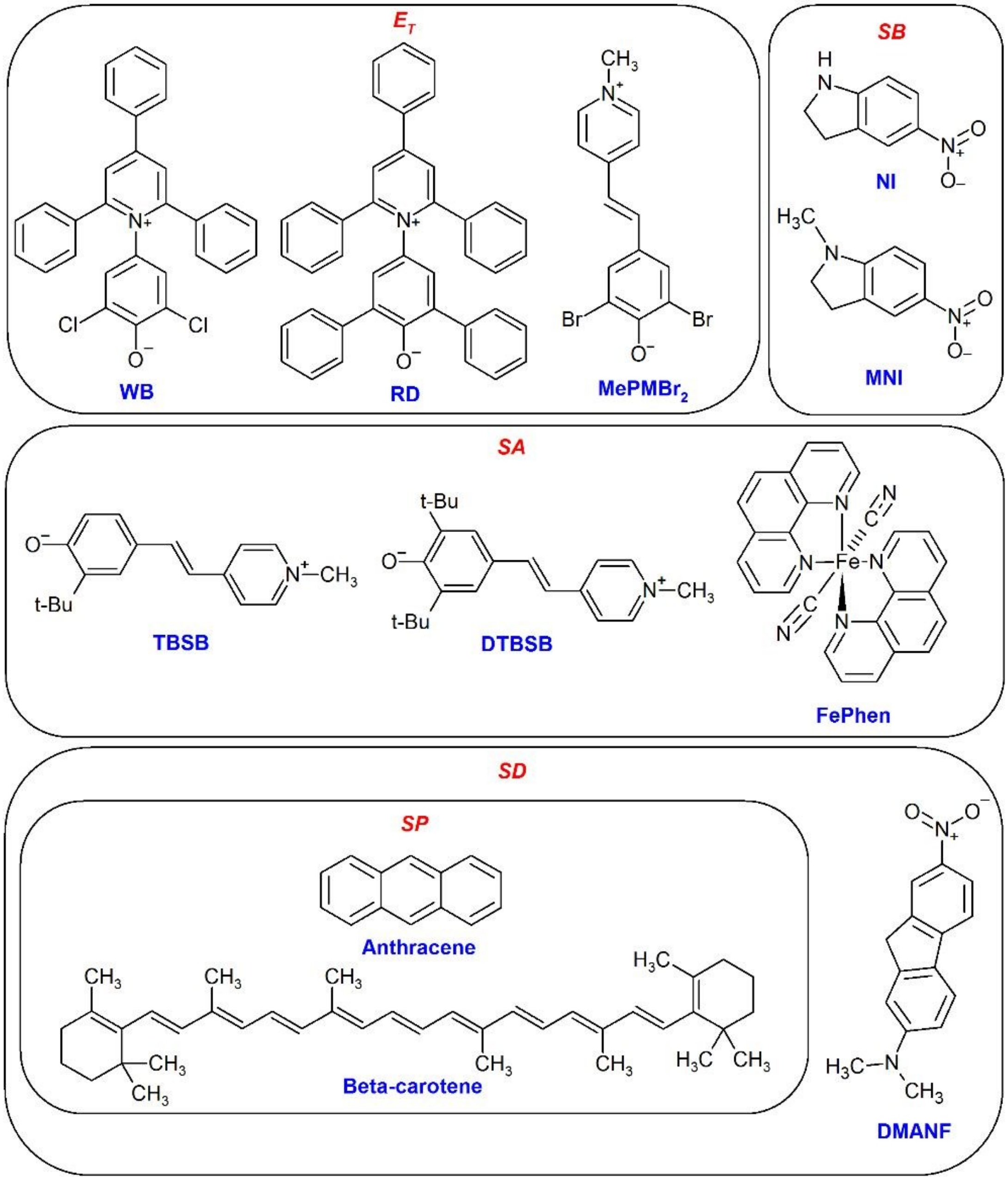

Figure 1: Molecular structures of the solvalchromic probes of interest in the present work. WB: 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate; RB: 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate; MePMeBr$_2$: 2,6-dibromo-4-[(*E*)-2-(1-methylpyridinium-4-yl)ethenyl] phenolate; TBSB: *o-tert*-butylstilbazolium betaine; DTBSD: *o,o'*-di-*tert*-butylstilbazolium betaine; FePhen: [Fe^{II}(1,10-phenanthroline)$_2$(CN)$_2$]; NI: 5-nitroindoline; MNI: 1-methyl-5-nitroindoline; DMANF: 2-(*N*,*N*-dimethylamino)-7-nitrofluorene; β-

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carotene: (all trans) 1,10-(3,7,12,16-tetramethyl-1,3,5,7,9,11,13,15,17-octadecanonaene-1,18-diyl)bis[2,6,6-trimethylcyclohexene].

RB (Reichardt betaine), NI, anthracene, and β-carotene were commercial (Aldrich), DMANF, MNI, DTBSB, TBSB, FePhen and WB (Wolfbeis betaine) were available from previous studies.[28-33]

2.3- Solvatochromic responses of the dyes: Uv-Vis spectroscopy

2.3.1- Preparation of the binary IL-DMSO mixtures

We weighed each IL in a volumetric flask; dried it under reduced pressure at 60 ^{o}C for 6h, and weighted it again. The mass of dry DMSO required to obtain $\chi_{\mathbf{DMSO}}$ = 0.6 was then introduced, and the mixture homogenized by (vortex) agitation.

2.3.2- Preparation of probe solutions in the IL-DMSO binary mixtures; Uv-Vis spectra recording, and refractive index measurements.

Stock solutions of the probes (0.036 mol/L) were prepared in acetone. We added 80 μL (most probes) or 150 μL (FePhen; WB) of the probe solution to glass vials with threaded capes (VWR 470151-622); evaporated the acetone; added 1 mL of the appropriate BM and dissolved the solid probe using a vortex mixer. The final probe concentrations were 2.88 x 10^{-3}, for all probes; 5.4 x 10^{-3} mol/L, for FePhen and WB.

We recorded each spectrum twice using Shimadzu UV-2550 UV-Vis spectrophotometer under the following conditions: Temperature 40 ± 0.05 ^{o}C (4000A digital thermometer, Yellow Springs Instruments), scanning rate = 160 nm/min; 0.5 cm path length cuvettes with PTFE stoppers. We calculated the values of $\lambda_{\mathbf{max}}$ of the solvatochromic peaks (i.e., longest wavelength) from the first derivative of the spectra (OriginLab 8 software). The uncertainty in $\lambda_{\mathbf{max}}$ was ≤ 0.5 nm, leading to ± 0.06 kcal/mol uncertainty in E_T(WB) (spectral range = 470 to 510 nm); ± 0.004 in *SA* (spectral range = 590 to 610 nm); ± 0.02 in *SB* (spectral range = 420 to 460 nm); ± 0.02 in *SD* (spectral range = 435 to 460 nm); ± 0.01 in *SP* (spectral range = 379 to 392 nm).

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We used Rudolph Research J357 digital refractometer (operating at 488 nm) to measure the refractive indices of IL-DMSO BMs (χ_{DMSO} = 0.6) at 40 ± 0.05 ^{o}C.

2.4- Calculations

2.4.1- Calculations of the solvatochromic parameters of the IL-DMSO binary mixtures

These were calculated as given elsewhere. We list in **Table 2** each solvatochromic property (descriptor), the equation employed, and the corresponding reference. Here λ_{max} corresponds to the wavelength maximum of the solvatochromic peak of the probe; ν is the corresponding frequency in cm^{-1}.

Table 2: List of the solvatochromic probes along with the equations employed to calculate the corresponding solvent descriptors.^{a}

Equation	Probe	Solvent descriptor	Equation	Reference
1	RB, WB $MePMeBr_2$	E_T(RB) E_T(WB) $E_T(MePMeBr_2)$	$28591.5/\lambda_{max}$	34 35
2	TBSB DTBSB	*SA*	$0.4\ \Delta\nu/1299.8$ $\Delta\nu = \nu_{TBSB} - (1.4049\ \nu_{DTBSB} - 6288.7)$	36
3	FePhen	*SA*	$(\nu_{max} - 16255)/3637$	37
4	NI, MNI	*SB*	$(\nu_{NI} - \nu_{MNI}) - 1570/-1735$	29
5	DMANF Anthracene	*SD*	$(\nu_{solvent} - \nu_{DMANF})/1611$ $\nu_{solvent} = 28224.6 - 4887.45\ SP$	38
6	β-carotene	*SP*	$(24402 - \nu_{\beta\text{-carotene}})/3672$	39
7	Anthracene	*SP*	$(27660 - \nu_{anthracene})/1612.7$	38

a- Values of E_T(RB) and E_T(WB) are in kcal/mol.

2.4.2-Caculation of the molar volumes (V_M) of the neat ionic liquids

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The values of V_M were calculated using the Molinspiration platform.[40] To ensure the reliability of the volumes calculated by this software, we calculated V_M for 16 ILs (**Table ESI-2**), based on their molar mass and density[41,42] and correlated these (experimentally based) values with those calculated by the above-mentioned software. We obtained the following equation; showing the reliability of the theoretically calculated values of V_M.

$$V_{M;\mathrm{Experimental}} = 5.94866 + 1.04052\, V_{M;\mathrm{Calculated}} \qquad N = 16;\ R^2: 0.99123 \qquad \textbf{Equation 8}$$

3- Results and Discussion

3.1- Relevance of solvatochromic data to dissolution of carbohydrates

The term solvatochromism refers to the effects of the solvent on the spectra, absorption or emission, of solutes (e.g., the probes shown in **Figure 1**) that are sensitive to a particular solute-solvent interaction. Effects of solvents, or solvent mixtures, on the values of $\lambda_{\mathbf{max}}$ of the solvatochromic peak is then manipulated to get information on *SA*, *SB*, … etc, see Table 2.[34] As Shown by Eq. 9, the solvent empirical polarity E_T(probe) is the sum of contributions from H-bonding terms (*SA* and *SB*), dipolar- (*SD*), and dispersive interactions (*SP*).[43]

$$E_T(\mathrm{probe}) = E_T(\mathrm{probe})_0 + \mathrm{a}SA + \mathrm{b}SB + \mathrm{d}SD + \mathrm{p}SP \qquad \textbf{Equation 9}$$

where the descriptors *(SA, SB, SD, SP)* are those defined above; a, b, d, and p are the corresponding regression coefficients. For conformity with other terms in Eq. 9, we use the symbol SD instead of SdP (used by Catalán),[43] to denote solvent dipolarity.

In using Eq. 9 we are interested in the sign and magnitude of the regression coefficients. The former indicates whether a phenomenon is favored or not (positive and negative sign, respectively) by a specific solute-solvent interaction mechanism, e.g., H-bonding. Comparison of the |magnitudes| of the regression coefficients shows their relative importance to the phenomenon in question, e.g., solvatochromism.

As argued in Introduction, the interaction mechanisms that contribute to E_T(probe) are precisely those considered relevant for the dissolution of carbohydrate polymers. This is the underlying reason for using solvatochromic parameters for assessing/predicting the efficiency of, e.g., ILs as carbohydrate solvents. In other words, information on the sign/magnitude of the

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regression coefficients of Eq. 9 can be fruitfully employed to predict whether an IL, or a family of ILs, should be good solvents for cellulose and other carbohydrate polymers.[19,15] An example of this prediction is that ILs with effective basicity (= $SB - SA$) in the range $0.35 < SB - SA < 0.9$ are expected to be good cellulose solvents.[44,45]

3.2- Choice of the solvatochromic probes

As shown in the authoritative book on solvents and solvent effects in organic chemistry,[34] and in a more recent review on the subject,[46] there is a myriad of probes employed for the calculation of solvent descriptors. The probes chosen are usually a matter of suitability for the determination, *vide infra*; convenience and, sometimes, availability. As an example, we successfully used commercially available β-carotene to calculate SP instead of the polyene employed by Catalán whose synthesis involves 15 steps.[39,47]

Before discussing the regression data, we comment briefly on the rationale for choosing the probes. We employed WB because its lower pKa in water than RB (= 8.65 and 4.78, for RB and WB, respectively),[32,34] makes it less prone to protonation, e.g. by *traces* of acidic impurity, *if present*, in the protic ILs. Note that E_T(WB) and E_T(RB) are linearly correlated (correlation coefficient = 0.9905, N = 32 MSs).[32]

To calculate specific properties, for example *SA*, a pair of homomorphic probes (e.g., TBSB and DTBSB) is usually employed. The first, TBSB, is sensitive to solvent Lewis acidity, in addition to non-specific interactions. The second, DTBSB, is sensitive only to non-specific interactions.[36] The value of *SA* is calculated by manipulating the spectral data of this pair of probes. We were unable to use TBSB to calculate *SA* because its dissolution in the BM resulted in disappearance of its solvatochromic peak. Schade *et al.* (2014) indicated the instability of the same probe in other imidazole-based ILs, due to an (unspecified) side reaction.[37] In agreement with their explanation; we found that the solvatochromic peak of TBSB was not recovered by addition of triethylamine (to deprotonate the probe). For calculation of *SA*, we employed the probe FePhen that is stable in acidic media. Note that calculated values of *SA* using FePhen are linearly correlated with *SA* calculated using TBSB and DTBSB.[37] Solubility problem of β-carotene in some of these BMs precluded its use to calculate *SP*. As shown elsewhere,[38] anthracene can be used

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for this determination. Catalán and Hopf (2004) showed that $\nu_{\textbf{Anthracene}}$ shows a linear correlation with the Lorentz-Lorenz function of the refractive index $f(n)$. This function, on the other hand correlates with *SP, i.e.,* $\nu_{\textbf{Anthracene}}$ correlates with *SP*.[48] Calculation of *SD* requires use of spectral data of DMANF and a polarizability probe, in our case anthracene.[38]

3.3- Correlation of the solvatochromic descriptors of IL-DMSO mixtures

Based on the data of **Table 1**, we calculated the above-mentioned descriptors for IL-DMSO mixtures at 40 ^{o}C and fixed $\chi_{\textbf{DMSO}}$ = 0.6. **Table 3** shows the correlations calculated. Note that the solvent descriptors employed in these correlations are in their *reduced* form, as shown by Eq. 10 below, where Solv = solvatochromic. Consequently, the values of every parameter vary from 0 to 1, *i.e., we can directly compare* the |magnitudes| of the regression coefficients. In the following discussion, we concentrate on part **I** of **Table 3**; we discuss part **II** of the same table later.

$$Reduced\ Solv\ value = \frac{(Solv\ parameter - minimun\ Solv\ parameter)}{(maximum\ Solv\ parameter -\ minimum\ Solv\ parameter)}$$

Equation 10

Table 3. Correlations of the empirical polarity E_T(probe) with the solvatochromic parameters *SA, SB, SD, SP*; and other solvent properties: the molar volume of neat IL (V_M); the Lorentz-Lorenz refractive index function f(n) of IL-DMSO. Part (I) is for ionic liquids-DMSO; Part (II) is for neat molecular solvents.

Entry	Number of solvents	Correlated parameters	Correlation equation	R^2; ΣQ^2
I- Correlations of the solvatochromic probes in ILs-DMSO,[a]				
1	**18**	E_T(WB) *vs. SA, SB, SD, SP*	E_T(WB) = +60.03(0.87) – 1.39(0.66) *SA* – 0.34(0.65) *SB* – 1.65 (0.81) *SD* – 1.79(0.85) *SP*	0.533 9.45
2	**18**	E_T(WB) *vs. SA, SB,* V_M, f(n)	E_T(WB) =+58.18(0.65) – 2.15(0.71) *SA* – 0.20(0.62) *SB* - 2.10(0.88) V_M – 0.70(0.94) f(n)	0.567 8.52
3	**13**	E_T(WB) *vs. SA, SB, SD, SP*	E_T(WB) =+54.28(0.70) + 3.74(0.59) *SA* + 0.86(0.35) *SB* + 0.52(0.49) *SD* + 0.19(0.46) *SP*	0.889 1.133
4	**13**	E_T(WB) *vs. SA, SB,* V_M, f(n)	E_T(WB) =+54.61(0.28) + 2.77(0.37) *SA* + 0.61(0.24) *SB* - 1.06(0.34)) V_M + 0.41(0.33) f(n)	0.939 0.593
II- Correlations of the solvatochromic probes in neat molecular solvents,[b]				
5	**23**	E_T(WB) *vs. SA, SB,* V_M, f(n)	E_T(WB) = +45.61(3.10) + 13.25(2.42) *SA* + 3.65(2.73) *SB* - 6.49(3.71) V_M + 0.42(2.87) f(n)	0.820 116.7
6	**23**	E_T(RB) *vs. SA, SB,* V_M, f(n)	E_T(RB) = +36.81(2.45) + 14.17(1.91) *SA* + 3.82(2.16) *SB* - 4.90(0.88) V_M + 0.70(2.26) f(n)	0.885 77.7
7	**23**	E_T(MePMBr$_2$) *vs. SA, SB,* V_M, f(n)	E_T(MePMBr$_2$) = +43.45(1.98) + 5.86(1.54) *SA* + 5.49(1.74) *SB* - 7.78(2.36) V_M + 2.29(1.82) f(n)	0.817 47.24

a- We calculated the solvatochromic data *for the binary mixtures* from measurements at 40 °C, at $\chi_{\mathbf{DMSO}} = 0.6$. R^2 and ΣQ^2 refer to the correlation coefficient, and the sum of the squares of the residuals, respectively.

b- Regression analysis based on the solvatochromic data of **Table ESI-3,** at 25 °C in. The values of V_M and $f(n)$ were calculated as given for ILs, and ILs-DMSO, respectively.

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We have two observations regarding entry 1 of **Table 3** that shows the results of correlation of E_T (WB) with the four solvatochromic probes for 18 BMs: the values of R^2 and ΣQ^2 are modest; except for the first term, $E_T(WB)_0$, the signs of the solvent descriptors are negative.

The first result may be due to inclusion of three classes of protic and aprotic ILs in the correlation. These are based on substituted imidazole, DBU and TMG. As argued elsewhere for an extensive series of neat ILs,[49] good correlations are obtained for families with the same cation (e.g., those based on imidazole) and different anions. The negative sign of *all correlation coefficient* cannot, however, be readily explained. Consider the effect of solvent Lewis acidity on the value of E_T(WB). For imidazole-based ionic liquids C2-***H*** of the diazole ring is relatively acidic,[50] and forms H-bonds with the phenolate oxygen of WB, as shown by ^{1}H and ^{13}C NMR.[51,52] This H-bond increases the energy of the intramolecular charge transfer in WB ($O^- \rightarrow N^+$), leading to a hypsochromic (i.e., a blue) shift of the corresponding peak, with a concomitant *increase* in E_T(WB). Therefore, an increase in *SA* of the solvent increases the value of E_T(WB), consequently the sign of the *SA* term should be positive; this is not the case (in entry 1 of **Table 3**).

Another factor that bears on the quality of the correlation is the uncertainty in the calculated solvatochromic parameters. This is a consequence of the magnitude of $\Delta\lambda$ (= largest λ_{max} - smallest λ_{max}) for a given probe within the 18 BMs studied (**Table ESI-4**). Values of $\Delta\lambda$ in nm are: 32.3, 16.0, 34.0, 29.4, and 3.1 for WB, FePhen, NI, MNI, and anthracene, respectively. The small $\Delta\lambda$ value for last probe and the fact that values of λ_{max} for 10 BMs lie between 380 and 381 nm, prompt us to verify whether the use of another physicochemical property related to SP would result in a better correlation.

Solvent effects on ν of β-carotene (used for calculation of *SP*)[39] in organic solvents,[53,54] and BMs[55,56] showed linear correlation with the solvent Lorenz-Lorentz refractive index function $f(n)$ (= $(n^2-1)/(n^2+2)$) , as shown in part A of **Figure ESI-1**. As mentioned earlier, there is a linear correlation between $\nu_{Anthracene}$ and $f(n)$.[48] Consequently, we determined the refractive indices of the BMs, and calculated $f(n)$. As the correlation of $\nu_{Anthracene}$ and $f(n)$ for the BMs is also linear (part B of **Figure ESI-1**), we decided to test this property instead of *SP*.

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As shown by entry 5 of **Table 2**, we use *SP* to calculate *SD*; any uncertainty in the former is carried over to the latter. Therefore, we sought another physiochemical property to use in the correlation, instead of *SD*. For a homologous series of ILs (1-alkyl-3-methyimidazolium bis(trifluoromethylsulfonyl)amide, alkyl = n-propyl, n-butyl, n-octyl, n-decyl), the values of E_T(RB) decrease as a function of increasing the length of the attached alkyl group (E_T(RB) = 51.9; 51.5; 51.1; 51.0, respectively), i.e., as a function of increasing the molar volume of the solvent, V_M.[57] Similar phenomena were observed for cellulose swelling by MSs, and its dissolution in ILs, two processes that are sensitive to the same biopolymer-solvent interactions as the solvatochromic probes, *vide supra*. Thus, cellulose swelling by a series of aliphatic alcohols (ethanol to n-octanol) and 2-alkoxyethanols (2-methoxyethanol to 2-(n-butoxy) ethanol decreases regularly (exponential decay) as a function of increasing V_M. Inclusion of the latter parameter in the correlation of cellulose swelling (wt%) with solvent descriptors lead to better correlations.[58] Likewise, cellulose dissolution (wt%) decreases as a function of increasing the values of V_M for a series of homologous DBU carboxylates,[4] and 1,3-disusbtituted imidazolium acetates.[21] Therefore, V_M is related to both E_T(RB) and cellulose dissolution efficiency. Note that values of V_M are related to solvent *SD*, as follows: For a series of MSs (**Table ESI-5**), there is a correlation between values of *SD* and the relative permittivity ε, see Part A of **Figure ESI-2**. For the same MSs, and also for a series of ILs (**Table ESI-6**) there is an inverse relationship between ε and V_M, (see Parts B and C of **Figure ESI-2).**[59,60] *Therefore, there is theoretical ground for employing* V_M and *$f(n)$ in the correlations instead of SD and SP, respectively*.

Entry 2 of **Table 3** shows that this substitution resulted in a slightly better correlation for the 18 BMs; the sign of the V_M descriptor is negative, as expected, based on the preceding discussion (effect of V_M on E_T(probe)). As entry 3 of **Table 3** shows, however, the quality of the regression increased noticeably when we restricted the ILs to the 13 imidazole-based series, and substantially when we used V_M and f(n) instead of *SD* and *SP*, respectively. More importantly, however, *the signs of all descriptors in entries 3 and 4 are the expected ones*. That is, the values of the empirical polarity of the BMs *increase* as a function of:

- Increasing the Lewis acidity, due to H-bonding of the solvent to the phenolate oxygen of WB in agreement with the results of NMR data,[50] and theoretical calculation of the

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solvation of the RB probe.[61] Catalán also showed a similar sensitivity to solvent Lewis acidity;[43]

- Increasing the Lewis basicity, due to electrostatic attraction of the acetate ion to the positive nitrogen of WB;
- Increasing *SD*, *SP* and f(n).
- Decreasing the molar volume of the solvent V_M.

Values of the regression coefficients indicate that solvent Lewis acidity is the dominant factor that affects its empirical polarity. The lower value of the regression coefficient of *SB* is presumably due to the fact that the quaternary nitrogen of WB (also the structurally similar RB) is sterically crowded,[61] and its charge is diffused in the ring.[62] We corroborate this conclusion convincingly by the regression data of entries 5 to 7 of **Table 3**. In these, we carried out correlations for 23 MSs, using 3 probes, WB and RB of similar steric crowding around the probe´s positive nitrogen (by two phenyl groups), and $MePMeBr_2$ where this crowding is absent. The ratios of the regression coefficients (b/a, Eq. 9) are 0.28, 0.27, and 0.94 for WB, RB, and $MePMeBr_2$, respectively. Based on this set of solvents, it is safe to conclude that the low sensitivity towards SB in entries 1-4 of **Table 3** *is steric hindrance*, i.e., solvent basicity is also important to solvatochromism, hence to biopolymer dissolution, in agreement with published data.[17] Entries 3 and 4 of **Table 3** shows the importance of solvent polarizability.

Taken together, these results confirm that solvent descriptors that affect E_T(probe) are the same that are relevant to cellulose dissolution. Consequently, using solvachromic descriptors as guidelines for assessing solvent efficiency (for carbohydrate dissolution) is justified. With this relationship confirmed, we are planning to test the correlation between these parameters and cellulose dissolution efficiency by the same binary solvent mixtures.

4-Conclusions

The aim of this work is to contribute to the understanding of solvent efficiency in dissolving cellulose. and carbohydrates in general. Because solvatochromism is sensitive to the same solute-solvent interactions that control carbohydrate dissolution, in particular, H-bonding and hydrophobic interactions, we correlated the empirical (or overall) solvent polarity, E_T(probe),

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and the descriptors of specific solute-solvent interactions. In agreement with previous data on pure ILs,[37,49] we found satisfactory correlations between E_T(WB) and the descriptors of IL-DMSO binary mixtures, especially if the ILs tested are limited to the same class of compounds, derived from 1-methyl- and 1,2-dimethylimidazole (13 ILs). The quality of the correlation is enhanced by keeping the H-bonding terms and substituting SD by V_M, and SP by f(n). This substitution eliminates the inherent uncertainties associated with calculation of SP, hence of SD. Whereas *SA* is important in all correlations, the relative importance of *SB* is underestimated because the positive nitrogen atoms in RB and WB are sterically crowded. We corroborated this conclusion by correlations of three probes in 23 MSs, WB, RB (steric crowding) and $MePMeBr_2$ (free of crowding). *In summary*, our results indicate that efficient solvents for cellulose, and presumably for chitin and starch, should be dipolar and efficient Lewis acids and Lewis bases. There is a delicate balance between the hydrophobicity of the cation and its molar volume that controls its proximity to the probe. Using solvatochomism for solvent efficiency screening for carbohydrate dissolution is an excellent choice. It saves labor and cost because, unlike the laborious biopolymer dissolution experiments, the solvatochromic measurements are relatively simple, accurate and require much less material.

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5-References

[1] E. Borbély, *Acta Polytech. Hung.*, 2008, **5** (3), 11-18.

[2] C. L. Mccormick, P. A. Callais, B. H. Hutchinson, *Macromol*, 1985, **18** (12), 2394-2401.

View Article Online
DOI: 10.1039/D0NJ02258F

[3] T. Heinze, S. Köhler, In *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*, ed. T. Liebert, T. Heinze, E. J. Kevin, American Chemical Society, Washington, 1033, 2010, Chapter 5, 103-118.

[4] H. Hanabusa, Y. Takeoka, M. Rikukawa, M. Yoshizawa-Fujita, *Aust. J. Chem.*, 2019, **72** (2), 55-60.

[5] D. C. Ferreira, M. L. Oliveira, T. A. Bioni, H. Nawaz, A. W. T. King, I. Kilpelainen, M. Hummel, H. Sixta, O. A. El Seoud, *Carbohyd. Polym.*, 2019, **212**, 206-214.

[6] Y. Huang, P. Xin, J. Li, Y. Shao, C. Huang, H. Pan, *ACS Sustain. Chem. Eng.*, 2016, **4**, 2286-2294.

[7] A. Xu, J. Wang, H. Wang, *Green Chem.*, 2010, **12** (2), 268-275.

[8] J. Zhang, L. Xu, J. Yu, J. Wu, X. Zhang, J. He, J. Zhang, *Sci. China Chem.*, 2016, **59** (11), 1421-1429.

[9] O. Kuzmina, J. Bhardwaj, S. Vincent, N. Wanasekara, L. Kalossaka, J. Griffith, A. Potthast, S. Rahatekar, S. Eichhorn, T. Welton, *Green Chem.,* 2017, 19 (24), 5949-5957.

[10] L. A. Ramos, E. Frollini, A. Koschella, T. Heinze, *Cellulose*, 2005, **12**, 607–619.

[11] G. T. Ciacco, D. L. Morgado, E. Frollini, S. Possidonio, O. A. El Seoud, *J. Bra. Chem. Soc.*, 2010, **21**, 71–77.

[12] Y. Cao, J. Wu, T. Meng, J. Zhang, *Carbohyd. Polym.*, 2007, **69**, 665–672.

[13] M. Abe, K. Sugimura, Y. Nishio, *ChemistrySelect*, 2016, **1**, 2474–2478.

[14] T. Heinze, O. A. El Seoud, A. Koschella, *Cellulose Derivatives. Synthesis, Structure and Properties*. Springer International Publishing, Berlim, 2018.

[15] M. Kostag, M. Gericke, T. Heinze, O. A. El Seoud, *Cellulose*, 2019, **26**, 139-184.

[16] F. M. Hämmerle, *Lenzinger Ber.*, 2011, **89**, 12-21.

[17] O. A. El Seoud, M. Kostag, K. Jedvert, N. I. Malek, *Macromol. Mater. Eng.*, 2020, DOI: 10.1002/mame.2019008.

[18] B. Lindman, G. Karlström, L. STIGSSON, *J. Mol. Liq.*, 2010, **156**, 76–81.

[19] O. A. El Seoud, M. Kostag, K. Jedvert, N. I. Malek, *Polymers*, 2019, **11**, 1917-1921.

[20] M. Clough, *Green Chem.*, 2017, **19** (20), 4754-4768.

[21] B. Lu, A. XU, J. WANG, *Green Chem.,* 2014, **16** (3), 1326-1335.

View Article Online
DOI: 10.1039/D0NJ02258F

[22] A. King, J. Asikkala, I. Mutikainen, P. Järvi, I. Kilpeläinen, *Angew. Chem.*, 2011, **50** (28), 6301-6305.

[23] M. Kostag, M, T. Dignani, M. C. Lourenço, T. A. Bioni, O. A. El Seoud, Holzforschung, 2019, 73, 1103–1112.

[24] D. Zhao, H. Li, J. Zhang, L. Fu, M. Liu, J. Fu, P. Ren, *Carbohyd. Polym.*, 2012, **87**, 1490-1494.

[25] A. Xu, Y. Zhang, Y. Zhao, J. Wang, *Carbohyd. Polym.,* 2013, **92**, 540-544.

[26] W. L. F. Armagero, C. L. L. Chai, *Purification of laboratory chemicals*. Elsevier, New York, 2016.

[27] V. Losetty, P. Matheswaran, C. Wilfred, *J.Chem. Thermodyn.*, 2017, **105**, 151-158.

[28] G. Saroja, Z. Pingzhu, N. P. Ernsting, J. Liebscher, *J. Org. Chem.*, 2004, **69**, 987-990.

[29] J. Catalán, C. Díaz, V. López, P. Pérez, J. De Paz, J. Rodríguez, *Liebigs Annales*, 1996, **11**, 1785-1794.

[30] J. Catalán, P. Pérez, J. Elguero, W. Meutermans, *Chem. Ber.*, 1993, **126**, 2445-2448.

[31] A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82** (12), 3000-3005.

[32] C. T. Martins, M. S. Lima, O. A. El Seoud, *J. Org. Chem*., 2006, **71**, 9068-9079.

[33] O. A. El Seoud, *Pure Appl. Chem.*, 2009, **81**, 697-707.

[34] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 2002.

[35] M. A. Kessler, O. S. Wolfbeis, **Chem. Phys. Lipids**, 1989, **50** (1), 51-56.

[36] J. Catalán, C. A. Díaz, *Liebigs Ann.***,** 1997, **1997** (9), 1941-1949.

[37] A. Schade, N. Behme, S. Spange, *Chem.: Eur. J.*, 2014, **20** (8), 2232-2243.

[38] J. C. Del Valle, B. F. García, J. Catalán, *J. Phys. Chem. B*, 2015, **119** (13), 4683-4692.

[39] C. Loffredo, P. Pires, M. Imran, O. A. El Seoud, *Dyes Pigments*, 2013, **96** (1), 16-24.

[40] Molispiration Cheminformatics, http://www.molispiration.com, (accessed October 2019).

[41] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data*, 2006, **35** (4), 1475-1571.

[42] G. R. Vakili-Nezhaad, A. M. Alaisaee, M. A. Aljabri, S. S. Albarwani, Z. K. Aljahwari, *Mater. Phys. Mech.*, 2017, **32**, 8-13.

[43] J. Catalán, *J. Phys. Chem. B*, 2009, **113** (17), 5951-5960.

[44] L. K. J.Hauru, M. Hummel, A. W. T. King, I. Kilpeläinen, H. Sixta, *Biomacromol.*, 2012, **13** (9), 2896-2905.

View Article Online
DOI: 10.1039/D0NJ02258F

[45] A. Parviainen, A. King, I. Mutikainen, M. Hummel, C. Selg, L. Hauru, H. Sixta, I. Kilpeläinen, *ChemSusChem*, 2013, **6** (11), 2161-2169.

[46] V. G. Machado, R. I. Stock, C. Reichardt, *Chem. Rev.*, 2014, **114** (20), 10429-10475.

[47] D. Klein, P. Kiliçkiran, C. Mlynek, H. Hopf, I. Dix, P. G. Jones, *Chem. Eur. J.*, 2010, **16**, 10507-10522.

[48] J. Catalán, H. Hopf, *Eur. J. Org. Chem.*, 2004, **22**, 4694-4702.

[49] S. Spange, R. Lungwitz, A. Schade, *J. Mol. Liq.*, 2014, **192**, 137-143.

[50] S. Sowmiah, V. Srinivasadesikan, M. C. Tseng, Y. H. Che, *Molecules*, 2009, **14** (9), 3780-3813.

[51] J. G. Dawber, R. A. Williams, *J. Chem. So. Faraday Trans.*, 1996, **82** (1), 3097-3112.

[52] M. Afri, H. E. Gottlieb, A. A. Frimer, *Can. J. Chem.*, 2014, **92** (2), 128-134.

[53] A. B. Myers, R. R. Birge, *J. Chem. Phys.*, 1980, **73**, 5314-5321.

[54] T. Abe, J-L. M. Abboud, F. Belio, E. Bosch, J. I. Garcia, J. A. Mayoral, R. Notario, J. Ortega, M. Posés, *J. Phys. Org. Chem.*, 1998, **11**, 193-200.

[55] P. M. Mancini, A. C. Pérez, L. R. Vottero, *J. Solution Chem.*, 2001, **30**, 695-707.

[56] P. M. Mancini, C. G. Adam, G. G. Fortunato, L. R. Vottero, *Arkivoc*, 2007, **16**, 266-80.

[57] C. F. Poole, *J. Chromatogr. A*, 2004, **1037**, 49-82.

[58] O. A. El Seoud, L. C. Fidale, N. Ruiz, M. L. O. D'Almeida, E. Frollini, *Cellulose*, 2008, **15**, 371-392.

[69] J. P. Liu, W. V. Wilding, N. F. Giles, R. L. A. Rowley, *J. Chem. Eng. Data*, 2010, **55**, 41-45.

[60] T. Singh, A. Kumar, J. Phys. Chem. B, 2008, 112 (41), 12968-12972.

[61] C. Chiappe, C. Pomelli, : A semiempirical study. Theorical Chemistry Acconts, v. 131, n. 3, p. 1-7, 2012.

[62] H. Weingärtner, *Z. Phys. Chem.*, 2006, **220**, 1395-1405.

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Understanding the efficiency of ionic liquids-DMSO as solvents for carbohydrates: Use of solvatochromic- and related physicochemical properties

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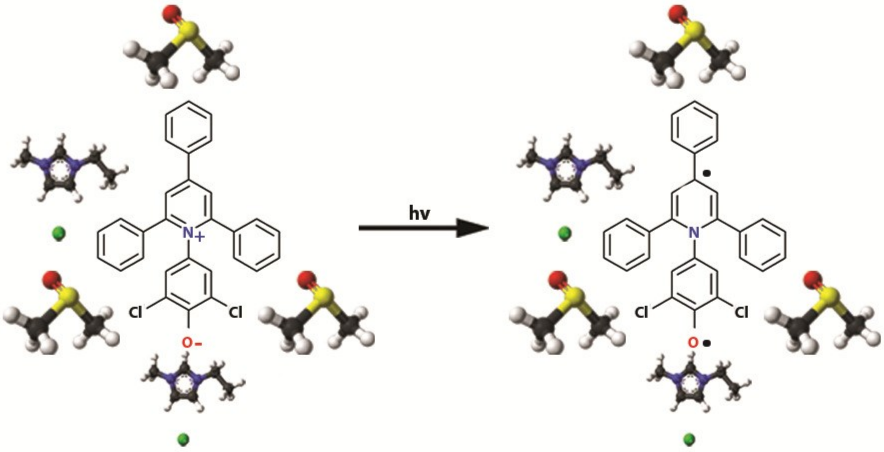

Quantification of interactions of solvatochromic probes with ionic liquids/DMSO serves as expedient approach for predicting solvent efficiency in dissolving carbohydrates