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# Measurement of the hydrogen bond acceptance of ionic liquids and green solvents by the $^{19}\text{F}$ solvatomagnetic comparison method

Christian Laurence<sup>a,\*</sup>, Sergui Mansour,<sup>b</sup> Daniela Vuluga,<sup>c</sup> Julien Legros<sup>b,\*</sup>

The  $^{19}\text{F}$  solvatomagnetic comparison method yields a more reliable scale ( $\beta_1$ ) of solvent hydrogen-bond acceptance than the solvatochromic comparison method. For  $[\text{C}_4\text{mim}]$  based ionic liquids, the  $\beta_1$  order  $\text{MeCO}_2^- (1.30) > \text{Cl}^- (0.79) > \text{NO}_3^- (0.67) > \text{SCN}^- (0.64) > \text{I}^- (0.44) > \text{BF}_4^- (0.36) > \text{PF}_6^- (0.27)$  is significantly correlated to the intrinsic hydrogen-bonding-, and even proton-, basicities of anions. For solvents of green interest, the  $\beta_1$  value of water is now settled down to 0.37, the newly determined value of limonene is 0.15, while those of  $\alpha$ -pinene (0.14), glycerol (0.36), Cyrene<sup>TM</sup> (0.40), 2-methyltetrahydrofuran (0.66), ethyl lactate (0.58), and  $\gamma$ -valerolactone (0.52) are found chemically more relevant than the solvatochromic ones.

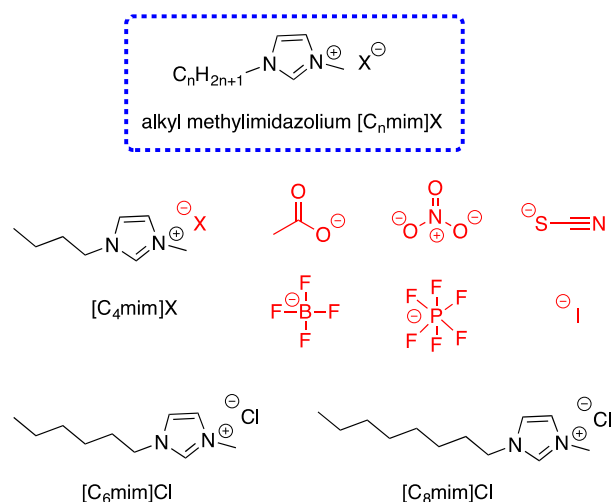
## Introduction

It is now well-recognized that the choice of the solvent in chemical and technological processes has a major impact on the ecological footprint of this process.<sup>1</sup> Since the solvent effect stems from solute/solvent interactions, it is essential to acquire a quantitative knowledge of these interactions. Thus, all ionic liquids (ILs) and most green solvents are hydrogen-bond acceptors (HBAs) by virtue of the negative charge on their anion and of non-bonding pair(s) on their heteroatom(s) or  $\pi$  bonding pair(s), respectively. If the solute is a hydrogen-bond donor (HBD), a solute HBD/solvent HBA hydrogen bonding takes place. This specific interaction has important consequences on the reactivity and physicochemical properties of the solute.<sup>2</sup> Thus, the HBA strength of these solvents must be quantitatively known.

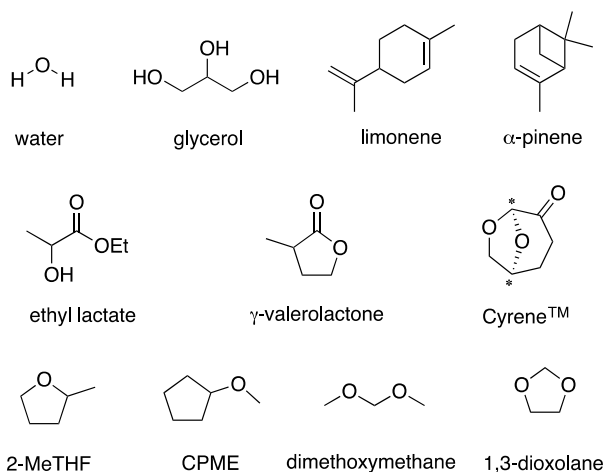
Today the most commonly used method for the determination of the HB acceptance of solvents is Kamlet-Taft's solvatochromic comparison method.<sup>3</sup> To build their  $\beta$  scale, these authors exploit the important bathochromic shifts of the  $S_0 \rightarrow S_1$  electronic transition of the HBDs 4-nitrophenol or 4-nitroaniline upon hydrogen bonding to HBA solvents and those of the similar non-HBD 4-nitroanisole and 4-nitro-*N,N*-diethylaniline in order to subtract the non-specific effects of the solvent. However, the two pairs 4-nitrophenol/4-nitroanisole and 4-nitroaniline/4-nitro-*N,N*-diethylaniline yield  $\beta$  values that differ significantly for a number of solvents,<sup>4</sup> the most dramatic difference being for tri-*n*-butylamine ( $\beta = 1.20$  and 0.49, for the OH and the  $\text{NH}_2$  probes, respectively)<sup>4</sup>, and the most serious for water, an important green solvent ( $\beta = 0.45$  and 0.16)<sup>4</sup> ( $\beta$  values commonly range from 0 to 1). For a series of ILs, Rani et al. observe that the 4-nitrophenol/4-nitroanisole pair gives "consistently higher values" than the 4-nitroaniline/4-nitro-*N,N*-diethylaniline pair (by amounts varying from +0.07 to +0.19).<sup>5</sup> In a review on solvatochromic parameters for solvents of interest in green chemistry,<sup>6</sup> Jessop et al. noted that "solvents that have been studied by more than one research group often have conflicting values". For the biomass derived solvents ethyl lactate and 2-

methyltetrahydrofuran (MeTHF), the  $\beta$  differences are 0.11 and 0.13, respectively,<sup>6</sup> and for 1-butyl-3-methylimidazolium acetate  $[\text{C}_4\text{mim}]\text{OAc}$  literature values range from 1.05 to 1.20.<sup>6</sup>

While the physical properties of solvents are well measured and not controversial,<sup>7</sup> empirical solvent parameters (here  $\beta$ ) are often assigned a wide range of conflicting values. This paper is intended to rectify this abnormal situation by using the recently designed  $^{19}\text{F}$  solvatomagnetic comparison method.<sup>4</sup> In a first part, the concept of the method is recalled. In a second section of this work, this approach is applied to eight methylimidazolium-based ILs, covering a wide range of basicity (see Scheme 1), and the reliability of the obtained solvatomagnetic  $\beta_1$  values is assessed by comparing them with various properties aiming at measuring the basicity of their anion. In the last part, the solvatomagnetic  $\beta_1$  values are determined for solvents of interest in green chemistry (depicted in Scheme 2), and they are compared to the literature solvatochromic conflicting  $\beta$  values, and to the existing reliable  $\beta_1$  values of compounds of similar structure.



**Scheme 1.** Structures of studied alkyl methylimidazolium ILs:  $[\text{C}_6\text{mim}]\text{Cl}$ ,  $[\text{C}_8\text{mim}]\text{Cl}$  and  $[\text{C}_4\text{mim}]\text{X}$  (with  $\text{X} = \text{AcO}$ ,  $\text{NO}_3$ ,  $\text{SCN}$ ,  $\text{BF}_4$ ,  $\text{PF}_6$ ,  $\text{I}$ ).



Scheme 2. Structures of solvents of interest in green chemistry.

## Results and discussion

### 1. The $^{19}\text{F}$ solvatomagnetic comparison method and the $\theta_1$ scale

The method exploits the sensitivity of the  $^{19}\text{F}$  chemical shift of 4-fluorophenol to the formation of a hydrogen bond between the OH group and HBA solvents.<sup>4</sup> Non hydrogen-bonding effects are subtracted from the global shift by means of the  $^{19}\text{F}$  chemical shift of 4-fluoroanisole, a molecule similar to 4-fluorophenol but non-HBD. In order to build a HBA solvent scale, three key steps are necessary:

1) the plot of the  $^{19}\text{F}$  chemical shift of 4-fluorophenol against that of 4-fluoroanisole for a series of eight quasi non-HBA solvents (heptane, cyclohexane, tetrachloromethane, trichloromethane, carbon disulfide, dichloromethane, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene). These solvents draw a reference line of eq (1) with a determination coefficient  $r^2$  close to 1 and a small standard deviation  $s$ , showing the similarity of non-hydrogen-bonding effects on the  $^{19}\text{F}$  chemical shifts<sup>4</sup>:

$$(1) -\delta(^{19}\text{F})_{\text{OH}} = 1.009 [-\delta(^{19}\text{F})_{\text{OMe}}] - 1.257$$

$$r^2 = 0.9992 \quad s = 0.025 \text{ ppm} \quad n = 8$$

where  $\delta(^{19}\text{F})_{\text{OH}}$  and  $\delta(^{19}\text{F})_{\text{OMe}}$  stand for the fluorine chemical shifts of 4-fluorophenol and 4-fluoroanisole, respectively.

2) the addition of data points representing HBA solvents to this graphic. It is found that they are all displaced from the reference line by an amount  $\Delta\delta$ . This quantity represents the contribution of the hydrogen bond to the chemical shift of 4-fluorophenol.<sup>4</sup> It is calculated by eq (2):

$$(2) \Delta\delta = [-\delta(^{19}\text{F})_{\text{OH}}] - \{1.009 [-\delta(^{19}\text{F})_{\text{OMe}}] - 1.257\}$$

3) the attribution of an origin and a format to define a solvatomagnetic  $\theta_1$  scale ranging from 0 to 1, a common practice for empirical solvent parameters. Following Kamlet and Taft<sup>3</sup> we set  $\theta_1 = 0$  for solvents (such as alkanes) obeying eq (1), and  $\theta_1 = 1$  for

hexamethylphosphorotriamide (HMPT) that deviates from the reference line by 3.041 ppm. Thus, the  $\theta_1$  parameter is calculated<sup>4</sup> by eq (3):

$$(3) \theta_1 = \Delta\delta / 3.041$$

With these origin and format,  $\theta_1$  can be compared to the solvatochromic  $\beta$  parameters of Kamlet-Taft type. The Figure 1 (drawn from data given below) illustrates the application of the solvatomagnetic comparison method to ILs and green molecular solvents.

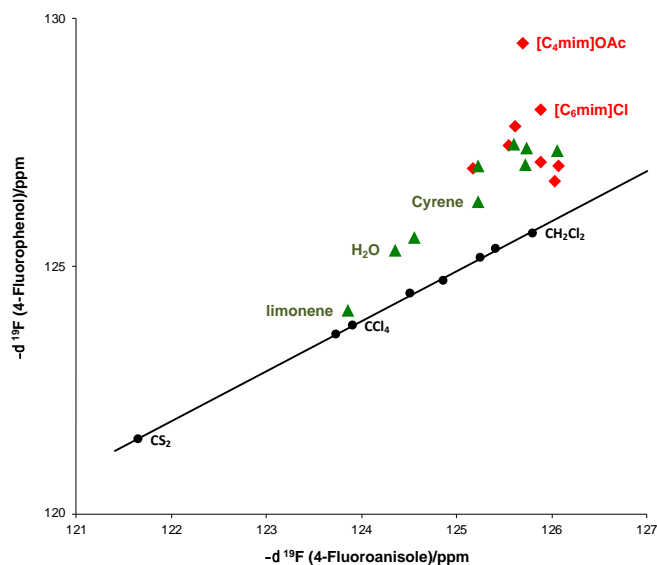


Figure 1. Solvatomagnetic comparison method. Negative of the  $^{19}\text{F}$  NMR chemical shift  $\delta$  of 4-fluorophenol plotted against negative of the chemical shift  $\delta$  of 4-fluoroanisole measured in various solvents. Non- or very weak HBAs fixing the reference line of eq 1: black circles. ILs: red diamonds. Green solvents: green triangles.

### 2. Solvatomagnetic $\theta_1$ values of ionic liquids

The  $^{19}\text{F}$  NMR results and the deduced  $\theta_1$  values are given in Table 1.

Table 1. Solvatomagnetic  $\theta_1$  scale (no unit) of HB acceptance of ionic liquids (ILs).<sup>a</sup>

Ionic liquids	$-\delta(^{19}\text{F})_{\text{OH}}$	$-\delta(^{19}\text{F})_{\text{OMe}}$	$\Delta\delta$	$\theta_1$
[C <sub>4</sub> mim]OAc	129.51	125.69	3.946	<b>1.30</b>
[C <sub>6</sub> mim]Cl	128.16	125.88	2.404	<b>0.79</b>
[C <sub>8</sub> mim]Cl	127.82	125.61	2.337	<b>0.77</b>
[C <sub>4</sub> mim]NO <sub>3</sub>	127.45	125.54	2.037	<b>0.67</b>
[C <sub>4</sub> mim]SCN	126.97	125.16	1.941	<b>0.64</b>
[C <sub>4</sub> mim]I	127.10	125.88	1.344	<b>0.44</b>
[C <sub>4</sub> mim]BF <sub>4</sub>	127.04	126.06	1.102	<b>0.36</b>
[C <sub>4</sub> mim]PF <sub>6</sub>	126.72	126.03	0.813	<b>0.27</b>

<sup>a</sup>  $^{19}\text{F}$  NMR chemical shifts  $\delta$  (ppm) of 4-fluorophenol ( $\delta(^{19}\text{F})_{\text{OH}}$ ) and 4-fluoroanisole ( $\delta(^{19}\text{F})_{\text{OMe}}$ ) are given with respect to neat  $\text{CFCl}_3$ .  $\Delta\delta$  (ppm) corresponds to the hydrogen-bonding contribution.

For the two room-temperature chloride-containing ILs, changing the length of the alkyl chain from hexyl to octyl decreases  $\beta_1$  by only 0.02 unit, so we consider that the HBA acceptance of  $[\text{C}_6\text{mim}]\text{Cl}$  can be safely compared to that of ILs of the  $[\text{C}_4\text{mim}]$  series.

The HBA solvatomagnetic scale of the ILs is illustrated graphically in Figure 2. The strongest measured neutral HB acceptor, piperidine ( $\beta_1 = 1.12$ ),<sup>8</sup> and the weakest one, chlorobenzene ( $\beta_1 = 0.06$ )<sup>8</sup>, are also shown for comparison. The strongest HBA IL,  $[\text{C}_4\text{mim}]\text{OAc}$ , exceeds piperidine, and the weakest one is  $[\text{C}_4\text{mim}]\text{PF}_6$ .

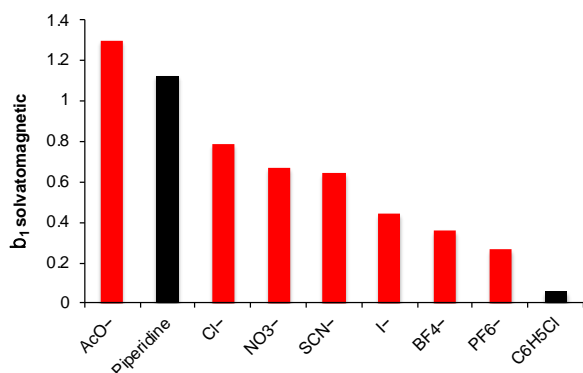


Figure 2. Solvatomagnetic  $\beta_1$  scale of  $[\text{C}_4\text{mim}]\text{X}$  ionic liquids (the neutral HBAs piperidine and chlorobenzene are shown for comparison in black).

Satisfactorily, we observed that the  $\beta_1$  scale is significantly correlated to two properties aiming to measure the intrinsic HB basicity of anions:

- the H-bond acceptor scale for anions constructed by Hunter and co-workers<sup>9,10</sup> from the H-bond formation constants  $K$  (as  $\lg K$  or  $\Delta G$ ) between tetrabutylammonium salts and three substituted phenols in the two solvents  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$ . The averaging of formation constants gives the  $\beta(\text{Hunter})$  scale.<sup>10</sup> 97.3% of the variance of the spectroscopic  $\beta_1$  scale is explained by this thermodynamic scale for 6 anions spanning a large basicity range from  $\text{CH}_3\text{CO}_2^-$  to  $\text{PF}_6^-$ . Figure 3 shows this correlation.

- the H-bond formation constants  $K$  (as  $\lg K$ ) between tetraalkylammonium salts and phenol in  $\text{CH}_2\text{Cl}_2$ .<sup>11</sup> Now, 92.6% of the  $\beta_1$  variance is explained by  $\lg K$  for 5 anions from  $\text{Cl}^-$  to  $\text{BF}_4^-$  (Figure 4).

In the same vein, the solvatomagnetic  $\beta_1$  scale is satisfactorily correlated ( $r^2 = 0.874$ ,  $n = 7$ ) to the hydrogen-bonding interaction energy  $E_{\text{HB}}$  in the equimolar  $[\text{C}_4\text{mim}]$ -anion mixture taken from COSMO-RS calculations<sup>12</sup> (Figure 5).

The most intrinsic scale of anion basicity is their proton basicity  $PA$ ,<sup>13-15</sup> the negative of the enthalpy change in the reaction of protonation of the anion *in the gas phase*. Hunter and co-workers have shown that their  $\beta$  scale for anions was not correlated to the *aqueous* proton basicity.<sup>10</sup> However, an excellent correlation ( $r^2 = 0.968$ ; Figure 6) is found between  $\beta_1$  and  $PA$  for 5 anions from the acetate to the iodide (no experimental values for the hexafluorophosphate and tetrafluoroborate anions being available<sup>15</sup>).

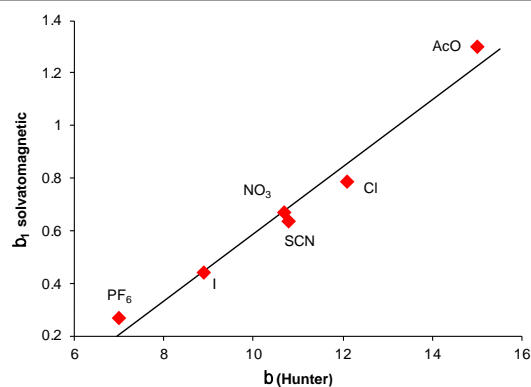


Figure 3. Correlation between the solvatomagnetic  $\beta_1$  values of  $[\text{C}_4\text{mim}]\text{X}$  ILs and the Hunter H-bond acceptor parameter for the anion  $\text{X}^-$ .

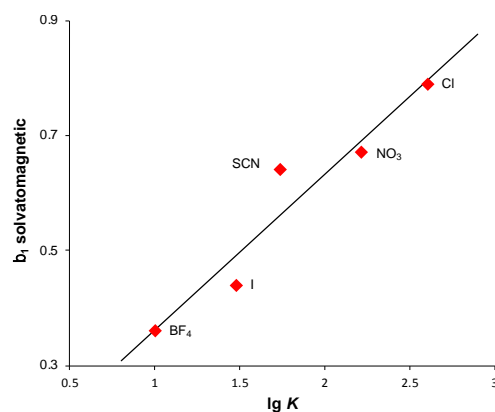


Figure 4. Correlation between the solvatomagnetic  $\beta_1$  values of  $[\text{C}_4\text{mim}]\text{X}$  ILs and the logarithm of the complexation constant  $K$  ( $\text{L mol}^{-1}$ ) for the hydrogen bonding of phenol to  $\text{NR}_4^+\text{X}^-$  in  $\text{CH}_2\text{Cl}_2$ .

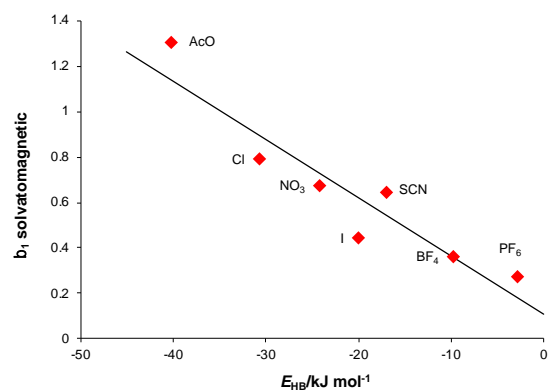
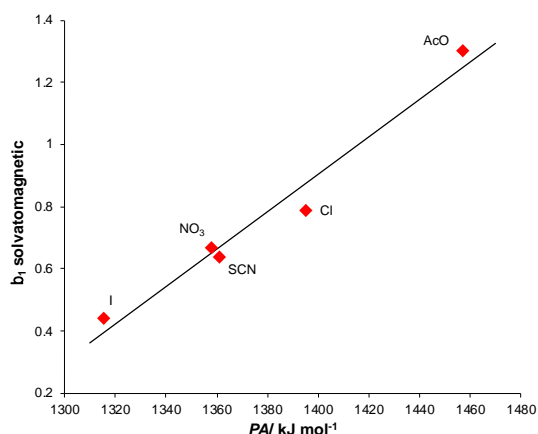


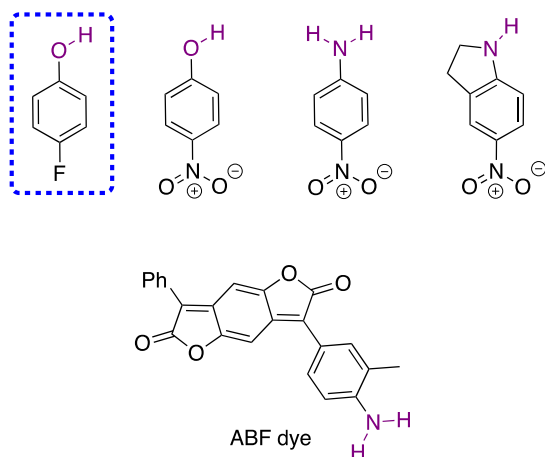
Figure 5. Correlation between the solvatomagnetic  $\beta_1$  values of  $[\text{C}_4\text{mim}]\text{X}$  ILs and their hydrogen-bonding interaction energy  $E_{\text{HB}}$  taken from COSMO-RS calculations.



**Figure 6.** Correlation between the solvatomagnetic  $\beta_1$  values of  $[C_4mim]X$  ILs and the proton affinity  $PA$  of their anion.

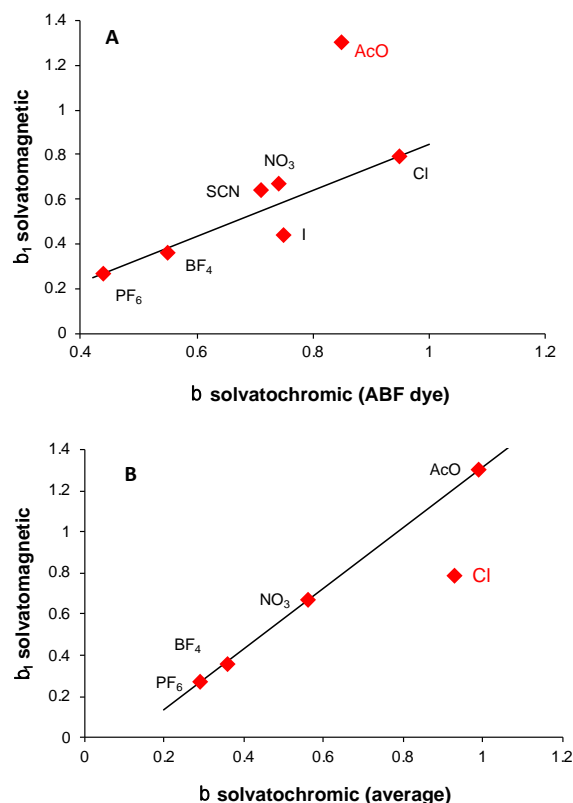
These correlations confirm that the HB acceptance of  $[C_4mim]$ -based ILs is strongly controlled by the intrinsic basicity of their anions. Above all, they validate the relative ILs HBA basicity order given by the solvatomagnetic comparison method.

We must now compare the solvatomagnetic  $\beta_1$  values to the solvatochromic  $\beta$  ones. A rigorous comparison is difficult to undertake because the solvatochromic  $\beta$ s are defined using procedures that are often different. Firstly, the solvatochromic HBD probes used are not always the same, and they may have quite different structures (Scheme 3). Secondly, subtracting the non-specific effects of the global solvatochromic shift to isolate the contribution of hydrogen bonding is made either using the solvatochromic comparison method (using similar non-HBD probes), or using linear solvation energy relationships<sup>16</sup> (a less rigorous method depending on the quality of non-specific parameters), or is not made at all (the raw shifts of the HBD probe are used). Thirdly, when the structure of the counter-cation is widely varied, the anion basicity may change. Lastly, the basicity range of studied anions not always spans from the very basic acetate to the poorly basic hexafluorophosphate.



**Scheme 3.** Structures of the solvatochromic probes 4-nitrophenol, 4-nitroaniline, 5-nitroindoline from left to right and, down, the ABF dye (the solvatomagnetic probe 4-fluorophenol is shown for comparison).

These difficulties limit the comparison to two sets of solvatochromic  $\beta$ s. Firstly, the results obtained<sup>17</sup> from the ABF dye for  $[C_4mim]$ -based ILs show an abnormal behavior of the acetate IL:  $r^2 = 0.556$  for 7 ILs but  $r^2 = 0.806$  when the acetate IL is excluded (Figure 7A). Secondly, the averaged solvatochromic  $\beta$  scale given by Jessop et al. in their review<sup>6</sup> shows that the  $\beta$  value for the chloride IL is overestimated:  $r^2 = 0.846$  for 5 ILs, but  $r^2 = 0.9998$  when the chloride IL is excluded (Figure 7B). The conflicting basicity orders between the two solvatochromic scales for the  $[C_4mim]OAc$  and  $[C_4mim]Cl$  ILs is noteworthy.

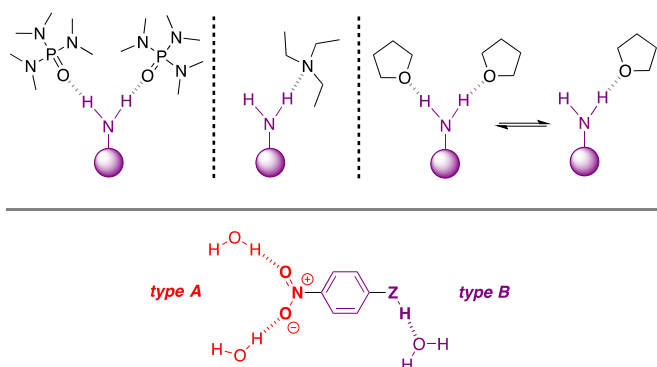


**Figure 7.** Comparison between the solvatomagnetic  $\beta_1$  values of  $[C_4mim]X$  ILs and (A) the solvatochromic  $\beta$  scale based on the ABF dye (the regression line does not take into account the acetate), and (B) an averaged solvatochromic  $\beta$  scale (the regression line does not take into account the chloride).

As a corollary, the solvatochromic  $\beta$  values appear less well correlated than the solvatomagnetic  $\beta_1$  ones to the intrinsic anion HB basicity. For example, the solvatochromic  $\beta$  values of ILs determined by the groups of Welton<sup>5</sup> and Spange<sup>17</sup> and those reviewed by Jessop et al.<sup>6</sup> are correlated to the intrinsic  $\beta$  (Hunter) HB basicity scale with determination coefficients  $r^2$  of 0.893 ( $n = 7$ ), 0.676 ( $n = 11$ ), and 0.921 ( $n = 5$ ), respectively, whereas  $r^2 = 0.973$  ( $n = 6$ ) for the solvatomagnetic  $\beta_1$  scale (vide supra).

These discrepancies between solvatomagnetic and solvatochromic scales are attributed to the solvatochromic one. Indeed, there are two shortcomings in the structure of the solvatochromic HBD probes. Firstly, the HBD groups of 4-nitroaniline and of the ABF dye are amino groups with two

N–H bonds. Vibrational spectrometry has shown that not only 1:2 hydrogen-bonded complexes, but also 1:1 complexes and a mixture of 1:2 and 1:1 complexes are formed with HBA solvents (Scheme 4-top).<sup>4</sup> There is no reason that this behavior cannot be extended to ILs. So, the bathochromic shifts upon hydrogen bonding, and consequently the solvatochromic  $\beta$  values, depend not only on the HB basicity, but also on the stoichiometry.<sup>4</sup> From this point of view, 4-nitroaniline and the ABF dye are less suitable indicators than 5-nitroindoline with a single N–H bond (Scheme 3). Secondly, in the amphiprotic solvents, all four solvatochromic probes are able simultaneously to accept H-bonds onto their nitro group or on the carbonyl groups in the case of the ABF dye (H-bond of type A, scheme 4-bottom) and to give H-bond of type B (scheme 4-bottom).<sup>3,4</sup> Both types of H-bonds lead to bathochromic shifts and the undesired type A effect cannot be satisfactorily subtracted from the total shift by the solvatochromic comparison procedure,<sup>3,4</sup> so that chemically unacceptable *negative*  $\beta$  values are found<sup>4</sup> for the most acidic alcohols and too high  $\beta$  values are found<sup>4</sup> for the most basic alcohols. This type A side effect can also contaminate the solvatochromic  $\beta$  values of ILs that contain C–H, N–H, or O–H HBD groups. For the ILs studied here, the C2–H group of the [C<sub>4</sub>mim] cation can give H-bonds to the nitro groups of 4-nitrophenol, 4-nitroaniline, 5-nitroindoline (and to their methylated compounds), and to the carbonyl groups of the ABF dye.



**Scheme 4.** Top: Stoichiometry of hydrogen bonding of the amino group. Vibrational spectroscopy shows<sup>4</sup> that 4-nitroaniline forms 1:2 complex with HMPT, 1:1 complex with triethylamine, and a mixture of 1:2 and 1:1 complexes with THF. Down: type-A (undesired) and type-B (desired) hydrogen bonds for 4-nitrophenol (Z = O) and 4-nitroaniline (Z = NH) in amphiprotic solvents (here water; for sake of clarity, the self-association of liquid water is not drawn). Both types of hydrogen bond produce bathochromic shifts on the S<sub>0</sub>→S<sub>2</sub> electronic transition of these indicators.

The 4-fluorophenol solvatochromic HBD probe is evidently devoid of the stoichiometric side effect, but also of the type-A hydrogen bond undesired effect, since the aromatic F atom is a very weak HBA site compared to the nitro and carbonyl groups.<sup>13</sup> It is therefore the probe of choice for the determination of the  $\beta$  parameter in hydrogen bonding studies.

### 3. Solvatochromic $\beta_1$ values of green solvents

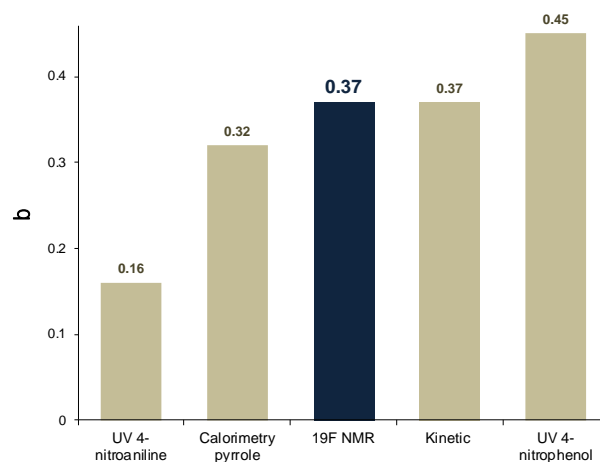
The <sup>19</sup>F NMR results and the deduced  $\beta_1$  values are given in Table 2.

**Table 2.** Solvatochromic  $\beta_1$  scale (no unit) of HB acceptance of solvents of interest in green chemistry.<sup>a</sup>

Solvents of interest in green chemistry	$-\delta(^{19}\text{F})_{\text{OH}}$	$-\delta(^{19}\text{F})_{\text{OMe}}$	$\Delta\delta$	$\beta_1$
Water	125.34	124.34	1.138	<b>0.37</b>
Glycerol	125.58	124.55	1.166	<b>0.38</b>
Limonene	124.12	123.85	0.412	<b>0.14</b>
$\alpha$ -pinene	123.98	123.69	0.434	<b>0.14</b>
Ethyl lactate	127.38	125.73	1.775	<b>0.58</b>
$\gamma$ -valerolactone	126.94	125.48	1.588	<b>0.52</b>
Cyrene™	126.31	125.22	1.220	<b>0.40</b>
2-MeTHF	127.46	125.59	1.997	<b>0.66</b>
CPME	127.02	125.22	1.930	<b>0.63</b>
Dimethoxymethane	127.05	125.71	1.466	<b>0.48</b>
1,3-Dioxolane	127.35	126.05	1.423	<b>0.47</b>

<sup>a</sup> <sup>19</sup>F NMR chemical shifts  $\delta$  (ppm) of 4-fluorophenol ( $\delta(^{19}\text{F})_{\text{OH}}$ ) and 4-fluoroanisole ( $\delta(^{19}\text{F})_{\text{OMe}}$ ) are given with respect to neat CFCl<sub>3</sub>.  $\Delta\delta$  (ppm) corresponds to the hydrogen-bonding contribution.

Till 2014, there was no accepted  $\beta$  value for water, the most important solvent. Indeed, in spite of a rigorous application of the improved solvatochromic comparison method,<sup>18</sup> the pairs of indicators 4-nitrophenol/4-nitroanisole and 4-nitroaniline/4-nitro-*N,N*-dimethylaniline yielded conflicting Kamlet-Taft  $\beta$  values of 0.45 and 0.16, respectively.<sup>4</sup> For the reasons evoked above (stoichiometry and type-A hydrogen bonds), both values are incorrect. In contrast, the correct value,  $\beta_1 = 0.37$ , could be obtained by the <sup>19</sup>F solvatochromic comparison method.<sup>4</sup> Interestingly, this value (and not the two solvatochromic ones) describes perfectly the solvent effect on the kinetic rate of a radical reaction that depends only on the HBA strength of solvents ( $r^2 = 0.996$ ,  $n = 4$  HBA solvents).<sup>4,19</sup> The solvatochromic value is also close to a value of 0.32 obtained from the enthalpy of solution of pyrrole in water.<sup>20</sup> The comparison of the literature  $\beta$  values with  $\beta_1$  is shown on Figure 8.



**Figure 8.** Comparison of the solvatochromic  $\beta_1$  value of water with literature values obtained by different methods. The incorrect solvatochromic values are found at both ends of the axe.

The solvatomagnetic comparison method yields also a value for glycerol,  $\beta_1 = 0.36$ , very different from literature solvatochromic values (range of 0.51 to 0.67).<sup>6</sup> This  $\beta_1$  value stands below those of the alcohols of the Pfizer green list solvents<sup>21</sup>: methanol (0.54),<sup>8</sup> ethanol (0.62),<sup>8</sup> 1-propanol (0.65),<sup>8</sup> 1-butanol (0.67),<sup>8</sup> 2-propanol (0.68),<sup>8</sup> and *tert*-butanol (0.73).<sup>8</sup> This low value can be explained by the presence of three electronegative (hence basicity decreasing) oxygen atoms in the glycerol structure and by a peculiar structuredness<sup>22</sup> of this highly viscous liquid.<sup>7</sup>

The solvatomagnetic  $\beta_1$  values of limonene (0.14), newly determined) and  $\alpha$ -pinene (0.14, this work) agree with the value of cyclohexene (0.14)<sup>8</sup> and with the well-recognized weak  $\pi$  carbon basicity of alkenes<sup>4,8,13</sup>. The literature solvatochromic  $\beta$  value of  $\alpha$ -pinene (0)<sup>6</sup> is in contradiction with all these results and is incorrect.

Ethyl lactate is a bifunctional HBA with ethyl ester and secondary alcohol functions. Its  $\beta_1$  value of 0.58 is logically placed between those of ethyl acetate (0.52)<sup>8</sup> and 2-propanol (0.68)<sup>8</sup>.

The bicyclic compound Cyrene<sup>TM</sup> (**dihydrolevoglucosenone**) is also polyfunctional with two ether oxygens and a carbonyl group. Its  $\beta_1$  value of 0.40 stands below that of 1,3-dioxolane (0.47, this work) and of cyclohexanone (0.55).<sup>8</sup> This value agrees with the electron-withdrawing, therefore decreasing-basicity, effects of the ether oxygens on the ketone function and of the carbonyl group on the dioxolane ring. The literature  $\beta$  value<sup>23</sup> of 0.61 does not reflect these substituent effects and is too high. Partly from this erroneous value, Cyrene<sup>TM</sup> has been suggested as a green replacement for *N,N*-dimethylformamide (DMF,  $\beta_1 = 0.69$ ). However, solvent similarity indexes<sup>24</sup> of Cyrene<sup>TM</sup> and DMF show that solvation of HBDS is not as good in Cyrene<sup>TM</sup> compared with DMF.<sup>24</sup> This conclusion agrees with our  $\beta_1$  value of Cyrene<sup>TM</sup> much lower than that of DMF.

The solvatomagnetic  $\beta_1$  value of the biobased  $\gamma$ -valerolactone (0.52) is higher than that of  $\gamma$ -butyrolactone (0.46)<sup>8</sup>, in agreement with the increasing-basicity effect of the methyl ring-substituent, and slightly lower than that of  $\delta$ -valerolactone (0.54)<sup>8</sup>, in agreement with the higher HB basicity of six-membered lactones compared to five-membered ones<sup>25</sup>. The literature solvatochromic  $\beta$  value<sup>6</sup> of 0.60 does not follow these structure-basicity relationships and appears too high.

The solvatomagnetic  $\beta_1$  values of the biomass derived ether, 2-methyltetrahydrofuran (MeTHF), ( $\beta_1 = 0.66$ ), and of the ether of green interest, cyclopentyl methyl ether (CPME), ( $\beta_1 = 0.63$ ), are significantly higher than the solvatochromic  $\beta$  ones (0.53 for 2-MeTHF, and 0.45 or 0.58 for CPME)<sup>6</sup>. In the family of alicyclic and aliphatic ethers, the solvatomagnetic CPME value agrees with that of *n*-butyl methyl ether (0.66), and that of 2-methyltetrahydrofuran is in accordance with that of tetrahydrofuran (0.58)<sup>8</sup> taking into account the electron-donating, therefore basicity-increasing, effect of the 2-methyl substituent. For dimethoxymethane, the till unknown solvatomagnetic  $\beta_1$  value of 0.48 is inferior to that of monoethers<sup>8</sup>, in agreement with the effect of the electronegativity of oxygen atoms on each other.

#### 4. Comparison of $\beta_1$ values to the Donor Number scale

A referee has suggested to compare  $\beta_1$  values to the Lewis basicity Donor Number (DN) scale (for a review on DN and an extensive compilation of values, see ref<sup>13</sup>). DN values are not available for the green solvents reported here, nor for any IL<sup>13</sup>. However, Schmeisser et al.<sup>26</sup> have claimed that the <sup>23</sup>Na NMR chemical shifts of NaClO<sub>4</sub> dissolved in ILs could provide a spectroscopic DN scale. The comparison of  $\beta_1$  with <sup>23</sup>Na chemical shifts does not show a general relationship ( $n = 7$ ,  $r^2 = 0.237$ ). However, the exclusion of the iodide and acetate-containing ILs rises the determination coefficient to 0.816. This behavior suggests a family-dependent  $\beta_1$  vs. DN relationship, as found by Taft et al.<sup>27</sup> for the Kamlet-Taft  $\beta$  vs. DN relationship for molecular solvents.

## Conclusions

The results reported herein can be summarized as follows:

- 1) This work offers to the ionic liquids and green solvent communities a reliable <sup>19</sup>F solvatomagnetic comparison method based on the HBD probe 4-fluorophenol. Whereas the solvatomagnetic comparison method rests on the same similarity principle than the solvatochromic one, the solvatomagnetic probe is not flawed by the shortcomings of the latter (variable stoichiometry of complexation, side effect of type-A hydrogen bonds).
- 2) Consequently, reliable  $\beta_1$  values are found for [C<sub>4</sub>mim]-based ILs spanning a large range of HB acceptance from [C<sub>4</sub>mim]OAc to [C<sub>4</sub>mim]PF<sub>6</sub>. This reliability is shown by the excellent to good relationships of  $\beta_1$  with the intrinsic basicity of anions measured by various properties: equilibrium constants for the hydrogen bonding of phenols to anions in various solvents, calculated energy of interaction between the [C<sub>4</sub>mim]<sup>+</sup> and the anion, and proton affinity of anions in the gas phase.
- 3) Finally, for most solvents of green interest studied, significant differences are found between solvatomagnetic  $\beta_1$  and solvatochromic  $\beta$  values. The  $\beta_1$  values are consistent with the well-established ones of the same chemical family, and better match with accepted structure-basicity relationships.

## Experimental section

### Chemicals

The purification of 4-fluorophenol was achieved by sublimation over P<sub>2</sub>O<sub>5</sub> and that of 4-fluoroanisole by vacuum distillation followed by drying on 4Å activated molecular sieves. ILs are commercial compounds. Their purity is: 99.5% ([C<sub>4</sub>mim]PF<sub>6</sub>), 98% ([C<sub>4</sub>mim]BF<sub>4</sub> and [C<sub>4</sub>mim]MeCO<sub>2</sub>), 97% ([C<sub>4</sub>mim]SCN, [C<sub>6</sub>mim]Cl, and [C<sub>8</sub>mim]Cl), 96% ([C<sub>4</sub>mim]I), or 95% ([C<sub>4</sub>mim]NO<sub>3</sub>). Green solvents are commercial compounds purified by standard methods.

### NMR measurements

<sup>19</sup>F NMR spectra were recorded on a 400 MHz spectrometer as previously detailed.<sup>4</sup>

### Statistics

The quality of correlations is judged by means of the determination coefficient  $r^2$  (square of the correlation coefficient), since 100  $r^2$  yields the percent of variance of the dependent variable explained by the explanatory variable. The values of  $r^2$  can be appraised as follows: excellent (1 to 0.95), good (0.95 to 0.90), satisfactory (0.90 to 0.85), fair (0.85 to 0.80), and poor (< 0.80).

### Conflicts of interest

There are no conflicts to declare.

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### References

- 1 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2015, **18**, 288–296.
- 2 C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 4<sup>th</sup> edition, 2011.
- 3 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027-6038.
- 4 C. Laurence, J. Legros, P. Nicolet, D. Vuluga, A. Chantzis and D. Jacquemin, *J. Phys. Chem. B*, 2014, **118**, 7594-7608.
- 5 M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831-16840.
- 6 P. G. Jessop, D. A. Jessop, D. Fu and L. Phan, *Green Chem.*, 2012, **14**, 1245-1259.
- 7 Y. Marcus, *The Properties of Solvents*, Wiley, Chichester, 1998.
- 8 C. Laurence, J. Legros, A. Chantzis, A. Planchat and D. Jacquemin, *J. Phys. Chem. B*, 2015, **119**, 3174-3184.
- 9 S. J. Pike and C. A. Hunter, *Org. Biomol. Chem.*, 2017, **15**, 9603-9610.
- 10 S. J. Pike, J. J. Hutchinson and C. A. Hunter, *J. Am. Chem. Soc.*, 2017, **139**, 6700-6706.
- 11 R. P. Taylor and I. D. Kuntz, *J. Am. Chem. Soc.*, 1972, **94**, 7963-7965.
- 12 A. F. M. Claudio, L. Swift, J. P. Hallett, T. Welton, J. A. P. Coutinho and M. G. Freire, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6593-6601.
- 13 C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales, Data and Measurements*, Wiley, Chichester, 2010.
- 14 P.J. Linstrom and W.G. Mallard, Eds., *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD (<http://webbook.nist.gov/chemistry>, accessed 2020)
- 15 J.-F. Gal, personal communication to C. Laurence (October 2020)
- 16 M.J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877-2887.
- 17 R. Lungwitz and S. Spange, *New J. Chem.*, 2008, **32**, 392-394.
- 18 P. Nicolet and C. Laurence, *J. Chem. Soc. Perkin Trans. II*, 1986, 1071-1079.
- 19 L. Valgimigli, K. U. Ingold and J. Lusztyk, *J. Am. Chem. Soc.*, 1996, **112**, 3545-3549
- 20 J. Catalán, J. Gomez, A. Couto and J. Laynez, *J. Am. Chem. Soc.*, 1990, **118**, 1678-1681.
- 21 K. Alfonsi, J. Golberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, *Green Chem.*, 2008, **10**, 31-36.
- 22 J.J. Towey, A. K. Soper and L. Dougan, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9357-9406.
- 23 J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C. R. McElroy, T. J. Farmer, T. Duncan, W. Raverty, A. J. Hunt and J. H. Clark, *Chem. Comm.*, 2014, **50**, 9650-9652.
- 24 M.D.Driver and C. A. Hunter, *Phys. Chem. Chem. Phys.*, 2020, **22**, 11967-11975.
- 25 F. Besseau, C. Laurence and M. Berthelot, *J. Chem. Soc. Perkin Trans II*, 1994, 485-489.
- 26 M. Schmeisser, P. Illner, R. Puchta, A. Zahl and R. van Eldik, *Chem. Eur. J.*, 2012, **18**, 10969-10982.
- 27 R. W. Taft, N. J. Pienta, M. J. Kamlet and E. M. Arnett, *J. Org. Chem.*, 1981, **46**, 661-667.