

## Investigation of the intrinsic electric field of nonhydroxyl and hydroxyl ionic liquids by vibrational Stark effect spectroscopy†

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Cite this: *RSC Advances*, 2013, 3, 11480

Received 14th March 2013,

Accepted 15th May 2013

DOI: 10.1039/c3ra41190g

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**Electric fields of ionic liquids (ILs) were investigated by vibrational Stark effect spectroscopy using ethyl thiocyanate as a probe molecule. It was found that the stretching vibration of C≡N in nonhydroxyl ILs originates exclusively from the intrinsic electric fields, which are on average 3.0 MV cm<sup>-1</sup> higher than those of molecular solvents. In contrast, in the case of hydroxyl functional ILs, hydrogen bonding as well as the electric field contribute to the IR shift of C≡N.**

Due to their unique physiochemical properties that differ substantially from molecular solvents, ionic liquids (ILs) have been extensively investigated as an interesting class of solvent media and even catalysts for both catalysis and synthesis.<sup>1–6</sup> Lots of reactions that have been carried out in/with ILs demonstrated better behavior than those in organic solvents including enhanced reactivity and/or selectivity.<sup>7–10</sup> Although attempts have been made to develop empirical solvent parameters as a means of realizing the unexpected behavior and performance, the concepts derived from molecular liquids or aqueous chemistry may not be adequate for ILs in rationalizing their unique characteristics.<sup>11,12</sup> The unique features possessed by ILs are still dubious and always attributed to the so-called “ionic liquid effect” or “ionic liquid environment”.<sup>13</sup> As ILs are liquid media composed solely of ions, it is anticipated that strong, long range Coulombic interactions are present in ILs. In fact it is obviously contradictory with the dipolar and short range forces that predominate in molecular solvents.<sup>14</sup> The strength of Coulombic interactions between solutes/ions and the intrinsic electric field of ILs is likely responsible for most of the desirable characteristics of ILs, such as negligible volatility, low melting point, and tunable solvation. It may also significantly affect the reaction equilibrium. However, up to now little is known about the intrinsic electric field of ILs. Therefore, measurement of the strength (magnitude) of the electric field in ILs is of great importance.

Vibrational Stark effect (VSE) spectroscopy is an experimental technique capable of measuring electric fields in proteins directly.<sup>15–17</sup> In VSE spectroscopy, the intrinsic response of a probe vibrational oscillator to its local electric environment is measured to estimate the magnitude and direction of the local electric field to which the probe is exposed.<sup>19</sup> The effect is described by the following equation:

$$\Delta\bar{E} = -\Delta\nu_{\text{CN}}^{\text{-obs}} / (\bar{\mu}_{\text{CN}} / hc) \quad (1)$$

Where  $h$  is Planck's constant,  $c$  is the speed of light,  $\Delta\bar{E}$  (MV cm<sup>-1</sup>) is the change of the protein's electric field, and  $\Delta\nu_{\text{CN}}^{\text{-obs}}$  (cm<sup>-1</sup>) is the observed frequency shift of the probe. The denominator ( $\bar{\mu}_{\text{CN}} / hc$ , cm<sup>-1</sup>/(MV cm<sup>-1</sup>)) is the characteristic linear Stark tuning rate of the probe,<sup>15–17</sup> a quantitative calibration of the sensitivity of the probe to the electric field.

VSE is often limited to an ordered (an isotropic, immobilized) system including a protein or a polymer matrix.<sup>16,18</sup> Boxer *et al.* have successfully applied this method to homogenous systems, such as conventional organic solvents, by ingeniously using the criteria that are based on the plot of the observed IR frequency *vs.* <sup>13</sup>C NMR chemical shifts.<sup>19</sup> Recently, we extended the VSE method to ILs and confirmed its validity in the direct evaluation of the electric field in ILs by using the same probe.<sup>20</sup> Based on the plot of nitrile stretching frequencies *vs.* <sup>13</sup>C chemical shifts, the obtained results indicated that the intrinsic electric fields in ILs are only slightly higher than those in common molecular solvents, but still comparable between these two media. In this work, a series of ILs (Fig. 1) with a wide variation in structure were investigated by the VSE method with a view to gaining a broader understanding of the influence of the cation, anion, and even the hydroxyl group on the electric field.

A range of probe-IL (1%, v/v) solutions were prepared by adding 10 μL EtSCN (ethyl thiocyanate) to 1 mL of IL inside an inert atmosphere glove box, and kept at room temperature overnight to attain a dissolution equilibrium; they were then subjected to spectral analysis. <sup>13</sup>C NMR spectra were collected using a double tube method without deuterated solvents, wherein a capillary tube (1.8 mm diameter) loaded with TMS was inserted

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† Electronic supplementary information (ESI) available: Materials and synthesis of ILs, spectroscopy measurements. See DOI: 10.1039/c3ra41190g

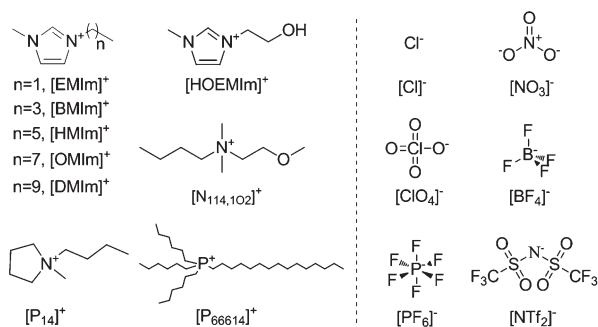


Fig. 1 Structures of the cations and anions investigated.

into a NMR tube with each IL as an external standard. A characteristic chemical shift of the C≡N of EtSCN ( $\delta(^{13}\text{C}_{\text{CN}})$ , label 1 in Fig. 2) in every case is not overlapped by those of ILs and gives rise to a distinct peak in the narrow range of 113.981–111.714 ppm. Fig. 2 shows the result of  $[\text{P}_{14}][\text{NTf}_2]$  as a representative example. EtSCN in nearly all of the ILs shows a single band for its C≡N stretching vibration ( $\nu_{\text{CN}}$ ), with a wide range from 2156.5  $\text{cm}^{-1}$  in  $[\text{HOEMIm}][\text{NTf}_2]$  to 2149.6  $\text{cm}^{-1}$  in  $[\text{BMIm}][\text{Cl}]$ , depending on the IL structure (Fig. 3 and Table 1).

At first we consider the case of 1-alkyl-3-methylimidazolium-based nonhydroxyl ILs. All  $\nu_{\text{CN}}$  bands in these ILs appear to be symmetric in shape and could be fitted to a single component by using the pseudo-Voigt function.<sup>21</sup> The full width at half maximum (FWHM) of the  $\nu_{\text{CN}}$  bands in all ILs are comparable ( $\sim 11 \text{ cm}^{-1}$ , Table 1), and are broader than the result of the thiocyanate probe in aprotic organic solvents (for example, acetonitrile, FWHM = 8.5  $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ , FWHM = 10.0  $\text{cm}^{-1}$ ).<sup>22</sup> It is known that the C≡N line shape is sensitive to the solvent dynamics, and the FWHM decreases with the average solvation time.<sup>22</sup> The higher FWHM of the C≡N stretching vibration in nonhydroxyl ILs is thus indicative of the slow solvation dynamics of ILs as compared to conventional solvents, which is indeed shown by the previous works.<sup>23,24</sup> The average solvation time in ILs is found to be three-orders higher than in conventional solvents.<sup>23,24</sup> The dataset of  $\nu_{\text{CN}}$  vs.  $\delta(^{13}\text{C}_{\text{CN}})$  in all the nonhydroxyl ILs considered in this work, as well as in organic solvents, are summarized in Fig. 4. As reported by Boxer *et al.*, the black solid line in Fig. 4 indicates the best fit for molecular solvents excluding

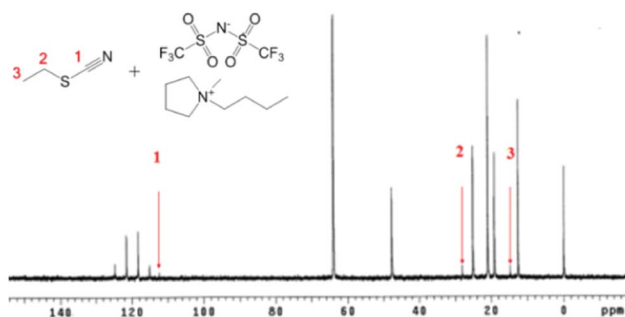


Fig. 2  $^{13}\text{C}$  NMR of EtSCN in  $[\text{P}_{14}][\text{NTf}_2]$  (1%, v/v).

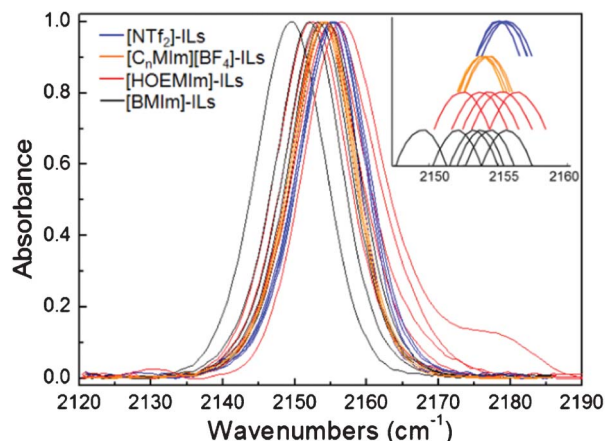


Fig. 3 Normalized IR absorption spectra of the  $\nu_{\text{CN}}$  in ILs (inset shows the enlarged and vertically shifted spectra for comparison).

H-bonding solvents ( $\text{H}_2\text{O}$  and formamide), and the gray region in Fig. 4 indicates the confidence interval derived from aprotic organic solvents.<sup>19</sup> As indicated by the arrows in Fig. 4, data points located above the confidence interval indicate strong H-bonding but a weak electric field, and *vice versa*. Evidently, nearly all the data points are located in the confidence interval.<sup>19</sup> Based on the criteria developed by Boxer *et al.* to distinguish whether the observed IR peak shifts of nitrile probes arise principally from changes in the local electric field or from both electric and chemical effects,<sup>19</sup> and on the earlier report,<sup>20</sup> it can be conjectured that the nonhydroxyl ILs containing C≡N resemble aprotic solvents, meaning their intrinsic electric fields could be determined by a VSE method. Careful fitting of the data of the ILs (excluding  $[\text{BMIm}][\text{Cl}]$ ) interestingly enables us to obtain a line with a slope ( $-1.70$ ) close to that of molecular solvents ( $-1.66$ ), but displaced by  $-2.19 \text{ cm}^{-1}$  (black dashed line in Fig. 4). Based on the Stark tuning rate of 0.72  $\text{cm}^{-1}/(\text{MV cm}^{-1})$ <sup>25</sup> of EtSCN, all nonhydroxyl ILs investigated have an average VSE electric field along the  $-\text{C}\equiv\text{N}$  bond axis quantitatively 3.0  $\text{MV cm}^{-1}$  higher than molecular solvents.

As it has been noted in Table 1, nonhydroxyl ILs possess VSE electric fields of about 3.5–8.3  $\text{MV cm}^{-1}$  less than  $[\text{BMIm}][\text{Cl}]$ ; this expanding range is even larger than the average difference between ILs and molecular solvents (3.0  $\text{MV cm}^{-1}$ ), but substantially smaller than the difference between ILs and molten salt NaCl as expected (*ca.* 150  $\text{MV cm}^{-1}$  as calculated by MD simulation<sup>20</sup>). In contrast to the obvious anion-dependence in  $[\text{BMIm}]$ -based ILs (3.5–8.3  $\text{MV cm}^{-1}$  lower than  $[\text{BMIm}][\text{Cl}]$ ),<sup>20</sup> the VSE electric field is less affected by the cation, as shown by the result of  $[\text{C}_n\text{Mim}][\text{BF}_4]$  ILs with a variable alkyl chain length and  $[\text{NTf}_2]$ -based ILs with various cation cores. Herein,  $[\text{NTf}_2]$  is chosen as the model anion because its low symmetry, bulky nature, and extensive delocalization facilitate the formation of low-melting ILs with a wide range of cations.<sup>26</sup> In the case of  $[\text{C}_n\text{Mim}][\text{BF}_4]$ , the VSE electric field only slightly falls down when lengthening the alkyl chain from ethyl to decyl (5.8–6.7  $\text{MV cm}^{-1}$  lower than  $[\text{BMIm}][\text{Cl}]$ ); a logical explanation for this phenomenon is that ILs,

**Table 1** NMR chemical shifts, vibrational frequencies, FWHM of  $\nu_{\text{CN}}$  in various ILs, and relative electric fields of nonhydroxyl ILs determined by VSE

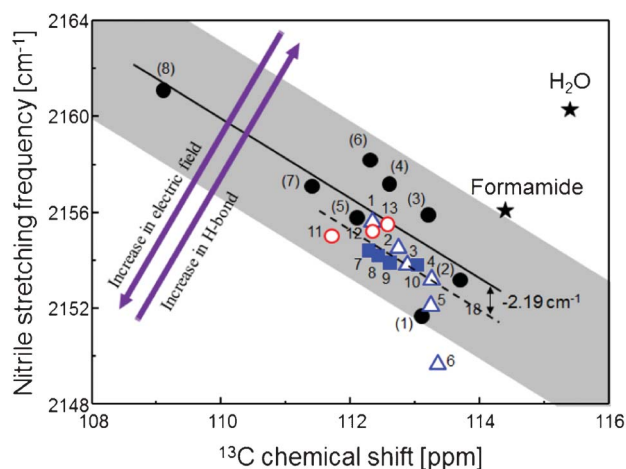
IL <sup>a</sup>	$\delta(^{13}\text{C}_{\text{CN}})$ [ppm]	$\nu_{\text{CN}}$ [cm <sup>-1</sup> ]	FWHM [cm <sup>-1</sup> ]	$\Delta\nu_{\text{CN}}^{\text{obs } b}$ [cm <sup>-1</sup> ]	$\Delta\bar{E}$ (VSE) <sup>c</sup> [MV cm <sup>-1</sup> ]
[BMIm][NTf <sub>2</sub> ]	112.343	2155.6	11.6	6.0	-8.3
[BMIm][PF <sub>6</sub> ]	112.746	2154.5	11.2	4.9	-6.8
[BMIm][BF <sub>4</sub> ]	112.887	2153.8	10.9	4.2	-5.8
[BMIm][ClO <sub>4</sub> ]	113.261	2153.2	11.3	3.6	-5.0
[BMIm][NO <sub>3</sub> ]	113.249	2152.1	11.1	2.5	-3.5
[BMIm][Cl]	113.375	2149.6	11.5	0	0
[EMIm][BF <sub>4</sub> ]	113.040	2153.8	10.7	4.2	-5.8
[HMIm][BF <sub>4</sub> ]	112.614	2153.9	10.7	4.3	-6.0
[OMIm][BF <sub>4</sub> ]	112.435	2154.2	10.6	4.6	-6.4
[DMIm][BF <sub>4</sub> ]	112.286	2154.4	10.8	4.8	-6.7
[P <sub>666,14</sub> ][NTf <sub>2</sub> ]	111.714	2155.0	9.9	5.4	-7.5
[P <sub>14</sub> ][NTf <sub>2</sub> ]	112.347	2155.2	11.1	5.5	-7.6
[N <sub>114,1O2</sub> ][NTf <sub>2</sub> ]	112.575	2155.5	11.5	5.9	-8.2

<sup>a</sup> VSE electric fields of [BMIm]-based ILs (excluding [BMIm][ClO<sub>4</sub>]) and [BF<sub>4</sub>]-based nonhydroxyl ILs are from ref. 20. <sup>b</sup> The observed frequency shifts relative to [BMIm][Cl]. <sup>c</sup> Relative electric fields (to [BMIm][Cl]) determined by VSE using EtSCN as a probe.

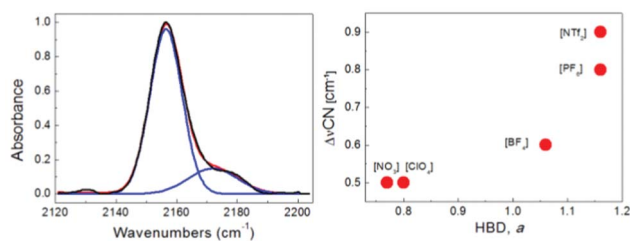
in particular those with long alkyl chain ILs, tend to aggregate and form separated polar charge and nonpolar tail domains.<sup>27</sup> Changing the cation core from imidazolium to ammonium, phosphonium, or pyrrolidinium, however, leads to an insignificant change in electric field, only  $-7.5$ – $-8.3$  MV cm<sup>-1</sup> with respect to [BMIm][Cl]. Among them, the imidazolium-based IL [BMIm][NTf<sub>2</sub>], possessing the highest charge delocalization, exhibits a slightly lower electric field than the others. [P<sub>666,14</sub>][NTf<sub>2</sub>], with a long alkyl chain and high steric hindrance which could help to shield its positive ionic centre, however,

unexpectedly exhibits the highest electric field, probably due to the different nature of the core atom.

When the substituting alkyl chain is functionalized by a hydroxyl tail, the resulting 1-(2-hydroxyethyl)-3-methylimidazolium-based hydroxyl ILs still exhibit  $\nu_{\text{CN}}$  bands with a symmetric shape towards EtSCN. This is except for [HOEMIm][NTf<sub>2</sub>], for which the  $\nu_{\text{CN}}$  could be deconvoluted into two components, a high-energy band at 2172.3 cm<sup>-1</sup> with a low shoulder at 2156.5 cm<sup>-1</sup>, as shown in Fig. 5. This result suggests that the spectrum of EtSCN in [HOEMIm][NTf<sub>2</sub>] is made up of two subpopulations due to different H-bonded conformers at the C≡N end. The high-energy component could be attributed to the formation of the specific H-bonded complexes, according to the C≡N stretching of methyl thiocyanate in trifluoroethanol.<sup>22</sup> The low-energy band, along with  $\nu_{\text{CN}}$  in other hydroxyl ILs (Table 2), shows a blue-shift ( $\Delta\nu_{\text{CN}}$ ) (0.5–0.9 cm<sup>-1</sup>) with respect to the C≡N stretching vibration in their respective [BMIm]-based nonhydroxyl ILs. This obvious frequency shift in hydroxyl ILs cannot be explained by a change in alkyl chain length (ethyl in hydroxyl ILs vs. butyl in nonhydroxyl ILs), since even in the case of [C<sub>n</sub>MIm][BF<sub>4</sub>] ILs, lengthening the alkyl chain from ethyl to hexyl only resulted in a 0.1 cm<sup>-1</sup> blue shift. It might be due to the presence of the OH, a better H-bonding donor than C–H,<sup>28,29</sup> that means the hydroxyl ILs are more likely to



**Fig. 4** Nitrile stretching frequencies vs.  $^{13}\text{C}$  chemical shifts of CN in ILs and molecular solvents (data of molecular solvents are from ref. 19, (1)-DMSO, (2)-DMF, (3)-acetone, (4)-CD<sub>2</sub>Cl<sub>2</sub>, (5)-THF, (6)-CDCl<sub>3</sub>, (7)-toluene and (8)-cyclohexane). Molecular solvents (●); [NTf<sub>2</sub>]-based ILs (○); [BF<sub>4</sub>]-based ILs (■); [BMIm]-based ILs (△). ILs: 1-[BMIm][NTf<sub>2</sub>], 2-[BMIm][PF<sub>6</sub>], 3-[BMIm][BF<sub>4</sub>], 4-[BMIm][ClO<sub>4</sub>], 5-[BMIm][NO<sub>3</sub>], 6-[BMIm][Cl], 7-[DMIm][BF<sub>4</sub>], 8-[OMIm][BF<sub>4</sub>], 9-[HMIm][BF<sub>4</sub>], 10-[EMIm][BF<sub>4</sub>], 11-[P<sub>666,14</sub>][NTf<sub>2</sub>], 12-[P<sub>14</sub>][NTf<sub>2</sub>] and 13-[N<sub>114,1O2</sub>][NTf<sub>2</sub>]. The black solid line indicates the best fit for molecular solvents:  $\nu_{\text{CN}} = -1.66 \delta(^{13}\text{C}_{\text{CN}}) + 2342.98$ ;  $R^2 = 0.68$ . The black dashed line indicates the best fit for nonhydroxyl ILs, ([BMIm][Cl]) and hydroxyl ILs not included):  $\nu_{\text{CN}} = -1.70 \delta(^{13}\text{C}_{\text{CN}}) + 2345.17$ ;  $R^2 = 0.56$ .



**Fig. 5** (Left) Normalized IR spectra of the C≡N stretching vibration of EtSCN in [HOEMIm][NTf<sub>2</sub>] and fitting of the C≡N stretching band by two pseudo-Voigt fits. The global fit is in red. (Right) Blue-shift of the C≡N stretching vibration ( $\Delta\nu_{\text{CN}}$ ) vs. the hydrogen bond donating acidity (HBD,  $a$ ) of hydroxyl ILs.

**Table 2** NMR chemical shifts ( $\delta(^{13}\text{C}_{\text{CN}})$ ), vibrational frequencies ( $\nu_{\text{CN}}$ ), FWHM, and hydrogen bond donating acidity (HBD,  $a$ ) in various hydroxyl ILs

IL <sup>a</sup>	$\delta(^{13}\text{C}_{\text{CN}})$ [ppm]	$\nu_{\text{CN}}$ [ $\text{cm}^{-1}$ ]	FWHM [ $\text{cm}^{-1}$ ]	$\Delta\nu_{\text{CN}}$ <sup>b</sup> [ $\text{cm}^{-1}$ ]	$a^c$
[HOEMIm][NTf <sub>2</sub> ]	113.280	2156.5	12.4	0.9	1.16
[HOEMIm][PF <sub>6</sub> ]	113.559	2155.3	13.9	0.8	1.16
[HOEMIm][BF <sub>4</sub> ]	113.559	2154.4	12.7	0.6	1.06
[HOEMIm][ClO <sub>4</sub> ]	113.981	2153.7	12.7	0.5	0.80
[HOEMIm][NO <sub>3</sub> ]	113.814	2152.6	11.9	0.5	0.77

<sup>a</sup> Data of [HOEMIm][Cl] are not available due to its solid state at room temperature. <sup>b</sup> Observed frequency shifts relative to the corresponding nonhydroxyl ILs. <sup>c</sup> HBD data from ref. 28.

behave as protic solvents, such as alcohols and protic ionic liquids.<sup>30</sup> Moreover, hydroxyl ILs with a less coordinative and nucleophilic anion, e.g., [HOEMIm][NTf<sub>2</sub>], give a higher  $\Delta\nu_{\text{CN}}$ . This anion-dependent  $\Delta\nu_{\text{CN}}$  is similar to the trend of hydrogen bond donating acidity (Table 2 and Fig. 5), in relation to the differentiating effect of hydroxyl on the strength of H-bonding.<sup>28</sup> As shown in Table 2, the much higher FWHMs of  $\nu_{\text{CN}}$  in hydroxyl ILs than those in nonhydroxyl ILs could be originated from the substantially slower solvation dynamics of hydroxyl ILs due to hydrogen bonding.<sup>29</sup>

Although the data points of  $\nu_{\text{CN}}$  vs.  $\delta(^{13}\text{C}_{\text{CN}})$  in all the hydroxyl ILs studied in this work still fall in the confidence interval, the observed IR shifts of the nitrile probe cannot be ascribed simply to the local electric field due to the aforementioned reasons. In contrast, most of the data points of the hydroxyl ILs are located above the fitting lines of molecular solvents (black solid line in Fig. 6) and nonhydroxyl ILs (black dashed line in Fig. 6), indicating a sharp contribution of H-bonding in comparison to that in nonhydroxyl ILs. Moreover, the fitting line of the  $\nu_{\text{CN}}$  vs.  $^{13}\text{C}$  NMR

data for hydroxyl ILs belongs to a slope ( $-4.77$ ) nearly identical to that obtained for nonhydroxyl ILs ( $-4.65$ ), but displaced by  $+4.5$   $\text{cm}^{-1}$  (Fig. 6). The consistent slope and positive offset are rather similar to the case of water–nitrile hydrogen bonds reported by Boxer,<sup>25</sup> with the only difference being that the displacement in ILs is much less than water ( $10$   $\text{cm}^{-1}$ ) and trifluoroethanol ( $\gg 10$   $\text{cm}^{-1}$ ).<sup>19</sup> This result strongly suggests that the H-bonding contribution and the electric effect in hydroxyl ILs are additive, but the H-bonding interaction of C=N and hydroxyl ILs is weaker than that for common protic solvents, which is not unexpected in view that the non-electric portion shift is reported to rely on the chemical identity of the H-bonding donor.<sup>19</sup>

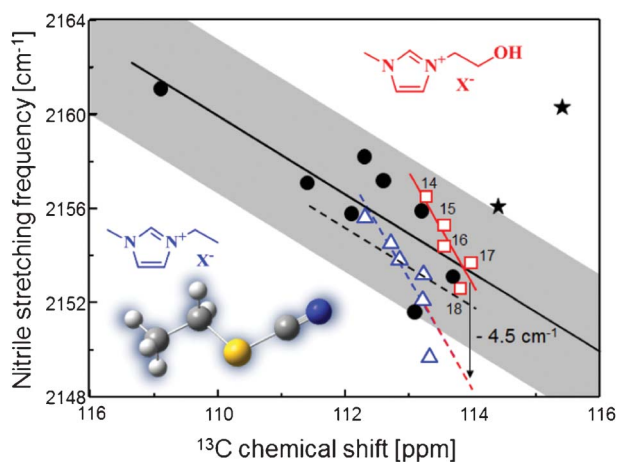
In conclusion, VSE as a simple experimental method is utilized successfully to evaluate the electric field of the nonhydroxyl and hydroxyl ILs. The observed IR shifts of the nitrile probe in nonhydroxyl ILs arise fully from changes in the local electric field, which are on average  $3.0$   $\text{MV cm}^{-1}$  higher than those of molecular solvents. While varying the IL structure, the cation core and alkyl chain play much less important roles than the anion. In hydroxyl ILs, the IR shift of the nitrile can be decomposed into both an H-bonding contribution and an electric field effect. Although the VSE method can only give a relative value, it indeed provides an easy approach to compare the electric fields between molecular solvents and ILs, and even ILs themselves. Moreover, the distinct response of C=N in turn underlines the substantial effect of the electric field on the solutes in ILs. Since the electrostatic interactions in ILs are essential for their manifold applications, our findings are of fundamental importance in the era of IL research.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21103208 and 21203219).

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**Fig. 6** Nitrile stretching frequencies vs.  $^{13}\text{C}$  chemical shifts of C=N in hydroxyl ILs with and without IR correction for H-bonding contribution. 14-[HOEMIm][NTf<sub>2</sub>], 15-[HOEMIm][PF<sub>6</sub>], 16-[HOEMIm][BF<sub>4</sub>], 17-[HOEMIm][ClO<sub>4</sub>] and 18-[HOEMIm][NO<sub>3</sub>]. Data points for other nonhydroxyl ILs are omitted for clarity. The blue dashed line indicates the best fit for [BMIm]-based nonhydroxyl ILs:  $\nu_{\text{CN}} = -4.65 \delta(^{13}\text{C}_{\text{CN}}) + 2678.10$ ;  $R^2 = 0.76$ . The red solid line indicates the best fit for hydroxyl ILs:  $\nu_{\text{CN}} = -4.77 \delta(^{13}\text{C}_{\text{CN}}) + 2696.67$ ;  $R^2 = 0.74$ . The red dashed line indicates the red solid line after subtracting a  $4.5$   $\text{cm}^{-1}$  correction for the hydrogen bonding.

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