PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Probing structural patterns of ion association and solvation in mixtures of imidazolium ionic liquids with acetonitrile by means of relative ^{1}H and ^{13}C NMR chemical shifts

Bogdan A. MAREKHA[1*], Oleg N. KALUGIN[2], Marc BRIA[3], Abdenacer IDRISSI[1]

[1]University of Lille – Science and Technology, LASIR (UMR CNRS A8516), Bat. C5, 59655, Villeneuve d'Ascq Cedex, France
[2]V.N. Karazin Kharkiv National University, Department of Inorganic Chemistry, Svoboda sq., 4, Kharkiv, 61022, Ukraine
[3]University of Lille – Science and Technology, CCM RMN, Bât. C4, Villeneuve d'Ascq 59650 France
Corresponding author: bogdan.marekha@univ-lille1.fr

Abstract

Mixtures of ionic liquids (ILs) with polar aprotic solvents in different combinations and under different conditions (concentration, temperature *etc.*) are used widely in electrochemistry. However, little is known about the key intermolecular interactions in such mixtures depending on the nature of the constituents and mixture composition. In order to systematically address the intermolecular interactions, the chemical shift variation of ^1H and ^{13}C nuclei has been followed in mixtures of imidazolium ILs 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$), 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$), 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate (BmimTfO) and 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BmimTFSI) with molecular solvent acetonitrile (AN) over the entire composition range at 300 K. The concept of relative chemical shift variation is proposed to assess the observed effects on a unified and unbiased scale. We have found that hydrogen bonds between the imidazolium ring hydrogen atoms and electronegative atoms of anions are stronger in $BmimBF_4$ and BmimTfO ILs than those in BmimTFSI and $BmimPF_6$. Hydrogen atom at position 2 of the imidazolium ring is substantially more sensitive to interionic hydrogen bonding than those at positions 4-5 in the case of BmimTfO and BmimTFSI ILs. These hydrogen bonds are disrupted upon dilution in AN due to ion dissociation which is more pronounced at high dilutions. Specific solvation interactions between AN molecules and IL cations are poorly manifested.

Introduction

Ionic liquids (ILs) are a subject of a rapidly expanding research field due to their numerous applications[1] and countless possible structures, combinations and functionalizations.[2] In many applications ILs are used in mixtures with molecular solvents of different nature.[1, 3] In particular, in the field of energy related electrochemical applications 1-alkyl-3-methylimidazolium ILs with perfluorinated anions (RmimX, X = BF_4^-, PF_6^- *etc.*) are typically combined with polar aprotic solvents such as acetonitrile (AN), propylene carbonate (PC), and γ-butyrolactone (γ-BL).[4-6] Originally, dilution of ILs in molecular solvents was considered as a simple mean to reduce their high viscosity for the sake of practical handling. However, not only does it increase the fluidity, but modifies the overall pattern of intermolecular and interionic interactions and the related properties, *e.g.*, electrical conductivity, [7-10] polarity,[5, 11, 12] diffusivity.[13-16] In terms of efficient practical use and development of novel IL-molecular solvent systems, the key fundamental issue is to establish a comprehensive microscopic picture on the structure and dynamics in such systems as a function of mixture composition and nature of the constituents.

In a rough approximation, mixtures of ILs with molecular solvents can be considered as electrolyte solutions[3] whose structure and properties are determined by the balance of such types of interactions as 'cation-anion', 'cation-cation' and 'anion-anion' that govern the existence of ion pairs and high order aggregates like $[Cat_nAn_m]^{-/0/+}$, and also by the 'cation-solvent', 'anion-solvent', and 'solvent-solvent' interactions. In this context, the peculiarity of binary systems based on ILs is that the composing ions are multiatomic and, in general, asymmetric. This implies that the mentioned above interactions should be regarded as anisotropic ones, having preferential localization around certain interaction sites. Another prominent feature of these systems, in comparison with conventional electrolyte solutions, is the full miscibility of ILs with many molecular solvents that allows obtaining mixtures ranging from dilute solutions of IL in molecular solvent to dilute solutions of molecular solvent in IL.[3]

In this regard, two main phenomena related to the redistribution of the balance between possible ion-ion, ion-molecular, and intermolecular interactions upon the composition change should be considered. They are ion association/aggregation and ion solvation. Going from neat IL to neat molecular solvent, these phenomena can be understood as a gradual destruction of large ionic aggregates (basic structure units of neat ILs) in favor of the smaller ones up to ion pairs, followed by complete dissociation into 'free' ions in very dilute solutions as a result of the interaction with solvent molecules.[3, 17] This interaction can be both specific (localized directional ion-molecular interactions) and non-specific (the effect of accumulation of significant amount of solvent which is capable of forming a medium similar to the neat solvent).

The phenomena of ion association and solvation manifest themselves at the microscopic level in the redistribution of electron density at the corresponding interaction sites. Among the currently known experimental methods that can reveal such effects, NMR[18, 19] and vibrational[19] (IR and Raman) spectroscopy should be highlighted as widely available and applicable (we emphasize here that NMR and vibrational spectroscopy are giving indirect information on the ion association and solvation processes). The former can bring out information on the change of the electronic microenvironment of every chemically non-equivalent nucleus and on the relative arrangement for some nuclei, whereas the latter probes the changes of dipole moment/polarizability/force constants, *i.e.*, the changes in the microenvironment of the atoms involved in the studied vibrational mode. In a broad perspective, NMR spectroscopy is more advantageous because it suffers from spectral overlaps and signal assignment much less than vibrational spectroscopy as it has been shown in our recent Raman study[20] and references therein.

Composition dependent NMR chemical shift variation has been used to address various specific interactions (mainly hydrogen bonding, but also stacking and C-H···π interactions) from the very beginning of extensive research on the first generation of chloroaluminate ionic liquids in 1980s.[21-23] The first thorough investigation of the variation of chemical shifts in mixtures of imidazolium ILs with molecular solvents was done by Avent *et al.*[24] They studied 1-ethyl-3-methylimidazolium halides (EmimCl/Br/I) in deuterated acetonitrile (AN-d_3) and dichloromethane (CD_2Cl_2) over a wide range of concentrations, as well as solutions in deuterated chloroform ($CDCl_3$) at a fixed concentration of 2 mol dm^{-3}. The observed ^{1}H and ^{13}C chemical shift variations were related to the particular sensitivity of the imidazolium ring CH sites and to the disruption of interionic hydrogen bonds in AN-d_3 and $CDCl_3$. A noticeable effect was also mentioned for the alkyl CH sites directly adjacent to the imidazolium ring. In the mixtures with low polar CD_2Cl_2, remarkably different concentration trends in chemical shifts were associated with the effect of pronounced aggregation of ion pairs in stacked anti-parallel motifs.

Another important study to mention was conducted by Bonhôte and colleagues[25] on a series of Emim$^+$ salts with anions of different basicity in deuterated acetone (Ac-d_6) over a wide range of concentrations. ^{1}H NMR chemical shifts of the alkyl signals were found to increase with dilution regardless of the anion. Similar downfield shift was also observed for the imidazolium ring CH signals for solutions of ILs with low basicity anions while in the case of anions of high basicity (containing the carboxylic group COO$^-$) cation's ring site signals showed pronounced chemical shift decrease, particularly at high dilutions. The results were interpreted in terms of the general non-specific deshielding dilution effects for all the cations' hydrogen atoms in the ILs with low basicity anions. The high basicity anions are considered as capable of forming strong hydrogen bonds with the imidazolium ring hydrogen atoms. Their disruption upon dilution of ILs with the solvent is the dominating contribution to the observed strong shielding of these protons. A possible influence of the aromatic ring stacking as a result of ion aggregation was also suggested.

Most of the published to date studies dealing with concentration dependence of chemical shifts in mixtures ‘imidazolium IL – polar molecular solvent’ did not cover a wide range of systems in a systematic manner. Among the most remarkable investigations on the influence of IL (imidazolium cation alkyl chain length and/or nature of the anion) or that of the solvent on the concentration trends of the chemical shifts of cations over the whole range of compositions it is worthy to mention studies on $RmimBF_4/PF_6$ in thiophene,[26] $RmimPF_6$ in Ac-d_6,[27] RmimTFSI in AN, MeOH, DMSO, and aromatic solvents,[28-31] $BmimBF_4$ with alcohols and amines,[32] $BmimPF_6$ in a set of polar aprotic solvents.[14] As a result, there is still no clear and comprehensive understanding of the influence of the nature of constituents of IL-solvent mixtures on the concentration trends in chemical shifts and, subsequently, on the underlying intermolecular interactions.

Problems of chemical shift referencing

The mentioned above lack of a unified model stems not only from rather scattered and poorly systematized literature data but also from different chemical shift referencing techniques employed. The latter issue causes significant problems in comparing different results in order to rationalize them in a single framework. Some authors even report neither the reference compound nor the referencing technique which makes this task even more complicated.[14, 33-36]

Even though ^{1}H-NMR chemical shift measuring has become a common technique to assess interactions in IL based systems, their accuracy has rarely been discussed. The main issue concerns chemical shift referencing. Since the concentration studies on mixtures of ILs with molecular solvents usually imply rather high concentrations, either a solvent signal or that of a reference compound, tetramethylsilane (TMS) or any other, cannot be regarded as non-influenced by the intermolecular interactions in the system. As a result, they cannot serve as an absolute reference in the so-called internal referencing procedure. Despite this obvious limitation there is an appreciable amount of studies based on interpreting the concentration induced variation of chemical shifts with internal referencing approach without appreciation of possible unaccounted interference. The most frequently employed internal reference compounds in such studies are TMS[27, 37-42] and residual non-deuterated solvent, *e.g.*, CD_2Cl_2[43, 44] or DMSO-d_6.[45]

External referencing technique allows one to avoid the problems of internal referencing and the use of deuterated solvents in the sample liquid. This is the most frequently used approach for IL-molecular solvent mixtures.[24, 26, 32, 46-48] In this technique, a coaxial capillary containing the reference compound and a deuterated lock-solvent is inserted into the NMR tube containing the sample itself. Just as in internal referencing, the deuterated solvent can serve as both lock-compound and chemical shift reference (due to residual protonated solvent molecules for ^{1}H-NMR). However, chemical shifts referenced in this way are inaccurate due to differences in bulk magnetic properties of the sample and of the contents of the capillary.[49, 50] The observed chemical shift, δ^{obs}, can be presented as follows:

$$\delta^{obs} = \delta^{real} + k(\chi_{sample} - \chi_{reference}) \qquad (1)$$

One can see that the correction term that connects δ^{obs} with the real value of chemical shift, δ^{real}, which reflects only the differences in shielding between the sample and reference nuclei, depends on geometrical properties of the insert, expressed as a geometrical factor, k, and on the difference in volume magnetic susceptibilities, χ, of the sample and reference media. In general, both geometrical factor and magnetic susceptibility differences are sample-specific. Indeed, the value of k is known *a priori* only for ideal geometrical shapes (sphere, infinite cylinder *etc.*) and in practice it is unique for each capillary and can be estimated in a separate experiment. At the same time, sample's magnetic susceptibility is a function of the composition and it may vary significantly.[51-52] Unfortunately, to the best of our knowledge, at present no systematic data can be found in the literature on magnetic susceptibilities of any ILs except for a narrow class of magnetic ionic liquids, where χ is one of the main characteristics,[53] and for EmimTFSI where it was estimated on purpose to correct for the magnetic susceptibility effects.[51]

As a result, one should be very cautious when interpreting concentration induced drifts of chemical shifts obtained in external referencing approach as they contain also the contribution due to the variation of the magnetic susceptibility correction. For the studies of ILs with molecular solvents, to the best of our knowledge, the magnetic susceptibility correction has been explicitly taken into account only in studies done by Takamuku *et al.*[28, 30, 31, 51, 54-56] They employed the so-called 'external double reference' method[57-59] in which a special capillary insert with a sphere blown out at its bottom is used. Reference compound gives two signals coming from molecules contained in the spherical and cylindrical parts of the capillary.[60] If the geometrical factor *k* of a given capillary has been calibrated in advance, then the separation between the two reference signals can be used to correct for the sample's magnetic susceptibility.[28, 30, 31, 51, 54-56]

In this study we present the results of a systematic investigation of ion solvation and association in binary mixtures of ILs with diverse perfluorinated multiatomic anions BF_4^-, PF_6^-, TfO^-, and $TFSI^-$ coupled with 1-butyl-3-methylimidazolium cation $Bmim^+$ (see Figure 1 for structures) and polar aprotic solvent AN (CH_3CN) by means of concentration dependent ^1H and ^{13}C NMR chemical shift analysis. To this end, we introduce an approach allowing following the ion solvation and association interactions via chemical shift monitoring on a unified scale. The approach is free of magnetic susceptibility correction issue and does not require sophisticated equipment. The rest of the paper is organized as follows: Experimental Section briefly describes the details of sample preparation, NMR measurements and auxiliary IR experiments; the approach of treating the chemical shift data is presented in the Concept of Relative Chemical Shift Variation; main results of relative chemical shift variations are given in the subsequent sections and finally, Conclusions are outlined.

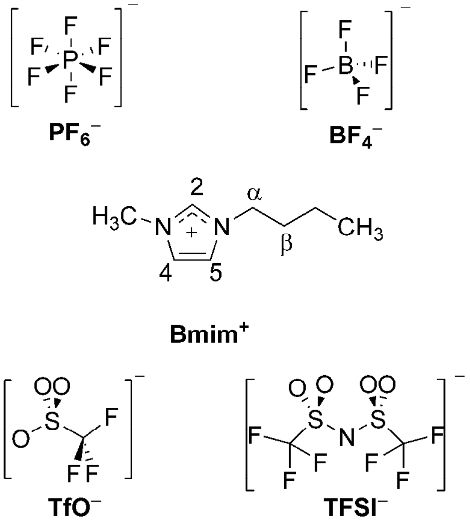

Figure 1. Chemical structures of the ions composing the four employed ionic liquids BmimBF$_4$, BmimPF$_6$, BmimTfO, and BmimTFSI

Experimental Section

The ILs 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF$_6$, CAS No. 174501-64-5), 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF$_4$, CAS No. 174501-65-6), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmimTfO, CAS No. 174899-66-2), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BmimTFSI, CAS No. 174899-83-3) were supplied by Solvionic (France) with a nominal purity of 99.5%. The content of water, halides, and methylimidazole, as estimated by the supplier, was < 500, 10 and 50 ppm, respectively. To minimize the effects of absorbed moisture, all RTILs were vacuum ($p < 10^{-6}$ bar) dried at 60 °C for at least 4 hours prior to the preparation of solutions as this procedure is known to lower the water content below 200–500 ppm. Acetonitrile (AN, CAS No. 75-05-8, Rotisolv, 99.9%, UV-IR grade, ≤ 100 ppm H_2O) was supplied by Carl Roth (Germany). It was additionally dried with activated 4 Å molecular sieves.

All solutions were prepared in glass vials by weight in an Ar-filled glovebox, where both the H_2O and O_2 contents were kept below 2.5 ppm (v/v). To accelerate mixing the solutions were sonicated for 30 minutes. Afterwards solutions were transferred into 5-mm o.d. NMR tubes (supplied by Wilmad-LabGlass) fitted with a coaxial insert containing D_2O as NMR-lock solvent and parafilmed. We employed a non-uniform concentration grid with more points taken around the composition corresponding to a distinct crossover in different properties of the mixtures, *e.g.*, in conductivity[7, 8, 61] and diffusivity[13] ($x_{IL} \sim 0.15$).

All NMR measurements were performed on a Bruker Avance-II 400 spectrometer (operating at magnetic field of 9.4 T) equipped with a 5-mm BBI probe with z-gradient. Sample temperature was kept constant at 300.0 ± 0.1 K by means of VT-2000 Bruker variable temperature unit which was calibrated with standard samples of 4% MeOH in MeOH-d_4 and 80% ethylene glycol in DMSO-d_6.[62] Prior to measurements each sample was thermally equilibrated in the probe's acquisition zone for at least 15 min. Broadband proton decoupling was employed during ^{13}C NMR spectra collection. Primary chemical shift referencing was performed at the level of spectrometer with respect to the signal of residual non-deuterated lock-solvent contained in the capillary insert. For further analysis, ^{1}H and ^{13}C chemical shifts were rereferenced to the signal of the terminal methyl group of the alkyl chain of butyl cation in neat ILs as explained in detail in the subsequent section.

FT-IR spectra were recorded at room temperature on a Bruker Tensor 27 spectrometer equipped with an ATR single reflection cell (ZnSe/diamond crystal) from Pike Technologies. Sample compartment was extensively flushed with nitrogen prior and during the measurements to avoid atmospheric water sorption. Each spectrum is an average of 128 scans with 2 cm^{-1} resolution.

Results and discussion

The concept of relative chemical shift variation

An approach which is free of magnetic susceptibility correction is based on referencing the chemical shifts to one of the signals from the sample without addition of internal reference compound. In this framework the observed chemical shift variation will reflect the relative concentration drift of the shielding of a given nucleus (*i.e.*, the real chemical shift) with respect to the reference one. Hoffmann and co-workers[63-66] used the terminal CH_3 of alkyl chain of $Rmim^+$ cation to reference proton chemical shifts in various mixtures of imidazolium IL with molecular solvents. They assumed on the basis of several conventional external referencing studies that the terminal methyl hydrogen atoms are the least polarizable and the changes in microenvironment upon dilution are weakly reflected in chemical shift variation (less than 0.1 ppm), as a result, the observed chemical shifts of the other hydrogen atoms can be considered as close to the real ones when referenced to the terminal methyl group signal. In other reports NCH_3 hydrogen atoms of $Emim^+$ cation were considered as unperturbed with addition of water and the corresponding signal was taken as reference.[15, 16]

Indeed, the real chemical shifts of terminal CH_3 and of NCH_3 hydrogen atoms that were measured by Takamuku and his colleagues vary by 0.3 ppm and 1.0 ppm, respectively, in DodecmimTFSI-C_6H_6 mixture,[30, 31] by less than 0.05 ppm each in DodecmimNO$_3$-D_2O/C_6D_6[56] and in EmimTFSI-H_2O,[51] by 0.05 ppm and 0.15 ppm in EmimCl-AN and by 0.07 ppm each in EmimTFSI-MeOH mixtures,[54] by ca. 0.2 ppm each in EmimTFSI-DMSO/AN mixtures.[28] The corresponding ^{13}C real chemical shifts, where they were reported,[28, 30, 31] exhibited variations of similar magnitude. Thus we may conclude that the choice of terminal methyl hydrogen atoms of $Rmim^+$ cations as internal ^1H and ^{13}C references is credible for a broad set of combinations ‘imidazolium IL-molecular solvent’. Nevertheless, it is only better than conventional internal referencing approach in the sense that the studied system is not perturbed by addition of a reference compound and *vice versa*.

With respect to the interpretation of such internally referenced chemical shift variations with changing concentration, it is noteworthy to mention the work of Li *et al.*[67] who clearly introduced and illustrated for EmimBF$_4$-H_2O system the concept of ‘relative chemical shift’, $\Delta\delta$, as the difference in chemical shifts between two different signals originating from the same compound at a given concentration. The corresponding concentration dependence of the relative chemical shift shows whether the nuclei of interest and reference ones experience the same changes in shielding when concentration is varied or there is some asynchronicity in the occurring changes of microenvironment of various nuclei. The same strategy was also used by Lyčka *et al.*[46] to follow the relative changes of ^{15}N chemical shifts of the imidazolium ring nitrogens for several neat RmimX ILs and for $BmimBF_4$ in several molecular solvents.

This approach is free of assumptions and does not require the reference to be an absolute one (*i.e.,* to be unaffected by changes in concentration). In contrast, the concentration trend in the relative chemical shift changes is essentially interpreted as a signature of discrepancy in behavior of nuclear shieldings of a given signal and the reference one as a function of concentration.

However, if one needs to address the concentration induced chemical shift variation for the entire set of signals of particular molecule this approach is impractical since the relative chemical shifts span over a broad range of values (1-10 ppm for ^{1}H and 10-150 ppm for ^{13}C for representative imidazolium IL-based systems) whereas the variations rarely exceed 1 ppm. In order to compare variations of all the signals, *i.e.*, to put them on the same scale, it is proposed to present chemical shifts (either relative or absolute) after subtraction of the corresponding values of chemical shifts at some reference concentration. The reference concentration can be chosen arbitrarily. So far the following options were proposed in the literature: a virtually intermediate concentration,[25] the lowest employed concentration,[36, 68] or the highest one.[14, 16, 27, 38, 69] However, from the point of view of interpretation, the most relevant reference concentration is that of the corresponding neat compound, and it is the most frequently used approach.[26, 32, 40, 41, 48, 70-74]

We combined the two ideas outlined above, *e.g.*, the relative chemical shift and the reference concentration in the concept of 'relative chemical shift variation'. It implies that the initial referencing should be done to one of the studied molecule's signal, terminal CH_3 for $Rmim^+$ cation and the most shielded group for a solvent (*e.g.*, CH_3 in AN, MeOH)

$$\Delta\delta_i^{\mathrm{CH_3}}(x) = \delta_i^{obs}(x) - \delta_{\mathrm{CH_3}}^{obs}(x) = \delta_i^{real}(x) - \delta_{\mathrm{CH_3}}^{real}(x) \qquad (2)$$

We note that our raw experimental data, which was initially externally referenced to the residual HDO in D_2O contained in the capillary insert, showed monotonic increase of ^{1}H and ^{13}C NMR chemical shifts of the terminal methyl group upon dilution in all the four studied systems by *ca.* 0.3-0.6 ppm. However, the magnitude of the magnetic susceptibility correction contributing to this value is unknown.

As it was mentioned above, thus referenced difference in the observed chemical shifts equals to the difference in real chemical shifts. These relative chemical shifts are then put on the same scale by subtracting the corresponding values of the neat substances:

$$\Delta\Delta\delta_i(x) = \Delta\delta_i^{\mathrm{CH_3}}(x) - \Delta\delta_i^{\mathrm{CH_3}}(x=1) \qquad (3)$$

Thus obtained values of relative chemical shift variation, $\Delta\Delta\delta_i\ (x)$, reflect how the real chemical shift difference between a given signal and the reference one (originating from the same molecule) changes with concentration. In fact, the relative order of the referencing procedures does not matter. Indeed, one can rewrite the expression for $\Delta\Delta\delta_i\ (x)$ in the following way:

$$\begin{aligned}&\Delta\Delta\delta_i(x) = \{\delta_i^{obs}(x) - \delta_{\mathrm{CH_3}}^{obs}(x)\} - \{\delta_i^{obs}(x=1) - \delta_{\mathrm{CH_3}}^{obs}(x=1)\} = \\ &\{\delta_i^{obs}(x) - \delta_i^{obs}(x=1)\} - \{\delta_{\mathrm{CH_3}}^{obs}(x) - \delta_{\mathrm{CH_3}}^{obs}(x=1)\}\end{aligned} \qquad (4)$$

From this expression it is clear that the value of $\Delta\Delta\delta_i\ (x)$ can be equally obtained by initial subtraction of the observed chemical shift values for the corresponding signal of neat component followed by the calculation of difference between the obtained values for a given signal and the reference one (*e.g.,* terminal CH_3). It is worth mentioning again that such treatment of the observed chemical shifts, which are normally referenced to residual protonated species of the lock compound contained in the external capillary, lead to results which are free of magnetic susceptibility correction. Moreover, as compared to external double reference method, the present one does not require additional calibrations, equipment and does not suffer from strong signal distortion due to capillary shape in the acquisition zone.

The second representation of the relative chemical shift variation shows that it can be regarded as the chemical shift drift of a given signal relative to the drift of a reference signal originating from the same molecule and we propose to stick to this style of interpretation.

In mixtures of imidazolium ionic liquids with molecular solvent, upon varying the concentration, it is the ion-ion and the ion-solvent interactions that mainly govern changes in electron density redistribution at molecular level. It is rather well established that these interactions are preferentially located at the imidazolium ring of cations while terminal methyl hydrogen atoms are hardly influenced.

Within the proposed approach of looking at the chemical shift changes we have summarized the literature observations on ‘imidazolium IL-molecular solvent’ systems which can be analyzed in this way (*i.e.,* where the observed absolute chemical shifts of the signals of interest, like those of the imidazolium ring hydrogen atoms, are published along with the terminal methyl group chemical shifts). The relative chemical shift variations $\Delta\Delta\delta_i\ (x)$ of the imidazolium ring hydrogen atoms were found to be negative in most of the studies which concern the following systems: RmimHal-H_2O,[63, 69, 74-76] R_1mimR_2CO_2-MeOH/H_2O,[16, 41] RmimMeSO_3-H_2O,[63, 64, 66] EmimEtSO_4-H_2O,[40] BmimBF_4-H_2O,[36, 77, 78] HexmimBr-Ac-d_6,[38] EmimTfO-Ac-d_6,[25] BmimBF_4-MeOH,[32] BmimOctSO_4-ethylene glycol,[79] BmimBF_4-AN,[48] EmimHal-AN,[24, 54] RmimBF_4/PF_6-thiophene,[26] DodecmimTFSI/NO_3-C_6H_6.[31, 56] Nevertheless, there are as well reports where the imidazolium ring hydrogen atoms exhibit more significant deshielding than the terminal methyl ones, *i.e.,* positive relative chemical shift variations are observed: EmimTFSI-Ac-d_6,[25] RmimPF$_6$/BF$_4$-Ac-d_6,[27] EmimTFSI-MeOH/DMSO/H_2O.[28, 51, 54] For some systems, however, there was no appreciable difference in chemical shift variation for the ring hydrogen atoms and the terminal methyl which resulted in roughly zero values of the relative chemical shift variations like in BmimBF$_4$-H_2O (note that there is a number of reports for this system concerning negative values of the relative chemical shift variation),[75, 76] and RmimBF$_4$-ethylene glycol.[79] There are several examples of rather peculiar behavior when H^2 and $H^{4\text{-}5}$ show opposite trends in their relative chemical shift variations. For HexmimTFSI in $CDCl_3$, H^2 was found to exhibit high positive values of $\Delta\Delta\delta_i\ (x)$ and moderate negative values for $H^{4\text{-}5}$,[65] similar observations were reported for EmimBF$_4$ in CD_2Cl_2,[80] while for BmimCl in DMSO the situation was inverse in signs.[69]

One can conclude that negative values of the relative chemical shift variation for the imidazolium ring hydrogen atoms are typically observed for ILs with rather basic anions which tend to form strong directional hydrogen bonds, *e.g.,* halides Hal$^-$, substituted sulfonates RSO_3^- and sulfates RSO_4^-, carboxylates RCO_2^- in various molecular solvents and for tetrafluoroborate BF_4^- based ILs. A separate class of systems which falls into this category deals with imidazolium ILs mixed with aromatic solvents where the negative relative chemical shift variations stem from significant shielding of the imidazolium hydrogen atoms interacting with aromatic π-electron density of the solvents.[26, 31, 56] Positive values are, in turn, observed for ILs with rather 'soft' large anions which have delocalized charge distribution like bis(trifluoromethylsulfonyl)imide TFSI$^-$, or hexafluorophosphate PF_6^- mixed with highly polar and donating solvents like MeOH, Ac or H_2O.

A common observation for all of the mentioned above studies on chemical shift variation in IL-solvent mixtures is that the most significant changes occur at low IL content (typically at $x_{IL} < 0.1$-0.2). Even more drastic changes were observed at higher dilutions ($x_{IL} < 0.05$-0.01) where the corresponding concentration range was studied.[30, 56, 63-65, 67, 69] As it was already mentioned by Dupont,[3, 17] under such high dilution regime the inherent IL-like ionic network is disrupted to ion pairs and other small aggregates and full dissociation into individual ions is occurring at the infinite dilution limit. In other words, under such conditions IL switch to conventional electrolyte-like behavior that is governed by the interplay between ion-ion and ion-molecular interactions.

Speculating about the cation ^{1}H chemical shift variation in mixtures of imidazolium ILs with molecular solvents, particularly with polar aprotic ones, three main effects may be put forward in order to explain the observed chemical shift variations which may be linked to distinct underlying intermolecular interactions.

- Firstly, in the case where there are no strong specific interactions between cation and anion, the general dilution effect, when a dipolar solvent does not establish specific interactions with IL and merely ‘lubricates’ the IL native network structure and then breaks it producing progressively smaller aggregate units up to full dissociation limit.[3, 17, 25] This effect is non-specific and it is equally applicable to all the atoms of IL over the entire concentration range. In terms of electronic effects, the increase of effective separation between IL ions caused by dilution should result in a general deshielding of the hydrogen atoms, *i.e.,* an increase of chemical shifts. However, as can be judged from the results of Takamuku *et. al.*[30, 31, 51, 54, 56] this effect rarely exceeds 0.05 ppm.
- Secondly, the effect associated with the specific interionic interactions. Indeed, for ILs these interactions are hydrogen bonds between the imidazolium ring hydrogen atoms, and to a lesser extent between the adjacent alkyl hydrogen atoms, from one side and the electronegative atoms of anions from the other side.[81-83] When these interactions are progressively disrupted by dilution, this leads to the shielding of the hydrogen atoms involved. The magnitude of this effect correlates with the strength of the hydrogen bond.[84]

- Thirdly, solvation of IL cations in polar molecular solvents can be mediated via formation of hydrogen bonds with donor atoms of the solvent molecules (*e.g.*, oxygen in alcohols, DMSO, Ac *etc.*; nitrogen in AN, amines *etc.*) in addition to non-specific ion-dipole interactions. Formation of such cation-solvent hydrogen bonds upon dilution of IL would contribute to deshielding of the imidazolium ring and of the adjacent alkyl hydrogen atoms.[28, 32, 42]

Apparently, the third and second effects are opposing each other and they are localized at the imidazolium ring and the adjacent hydrogen atoms. Hence, when referencing to the terminal methyl hydrogen atoms which are only prone to the first, non-specific effect, the net observation on the relative chemical shift variation of the hydrogen atoms of the imidazolium ring should reflect the balance between the second and third effects. In particular, when $\Delta\Delta\delta_i(x) > 0$ for the imidazolium ring hydrogen atoms, *i.e.,* effective deshielding, this can be interpreted as that hydrogen bonds established with solvent molecules are stronger than those broken between the IL cation and anion. If the relative chemical shift values are close to zero (as a tentative threshold we propose to use ±0.05 ppm as estimated for the real chemical shift drift of terminal methyl group of $Rmim^+$ by Takamuku et al. [30, 31, 51, 54, 56]), then the hydrogen bonds of cations with solvent molecules and with anions are of comparable strength. A situation in which neither the cation-solvent hydrogen bonds are formed nor the cation-anion ones are disrupted is hardly plausible for mixtures of imidazolium ILs with polar aprotic solvents. Last but not the least, negative relative chemical shift variation values $\Delta\Delta\delta_i(x_{IL}) < 0$ would suggest that the interionic hydrogen bonds are stronger than cation-solvent ones. We stress, that this conclusion has nothing to do with ‘absolute’ strength of the corresponding hydrogen bonds. Indeed, this conclusion can be drawn, for example, when a strong interionic bond is disrupted and an intermediate one is established with solvent and, equally, when a moderate hydrogen bond between the counterions is replaced with a very weak one with solvent. There is a particular case of large negative values $\Delta\Delta\delta_i(x_{IL}) \ll 0$ which can be attributed to the very strong interionic hydrogen bonds and rather weak ones between cation and solvent molecules. This is exactly the case of many systems with ILs with highly basic anions which form rather strong interionic hydrogen bonds.

Relative chemical shift variation in AN

All the spectra recorded in the present study (see for example spectra of the neat ILs in Figure 2) exhibit a single set of resonances which is an indication of effective averaging of all the possible equilibria at the NMR timescale of our experiments. In the mentioned above studies where the chemical shift variations in IL-solvent mixture was interpreted as a reflection of ion association equilibria, there was typically a single observed signal that was treated as a population averaged one between the associated and 'free' species. This seems logical since tentative ion-pair lifetimes are considered to be in the (sub)nanosecond range,[19] while a signal separation of 0.1 ppm in ^{1}H-NMR spectrum recorded on a 400 MHz instrument would require the corresponding species lifetime to be not less than *ca*. 6 ms.[85] Nevertheless, Tubbs and Hoffmann[86] observed two sets of signals in ^{1}H-NMR spectrum of EmimTFSI dissolved at a fixed concentration in a mixed solvent $CDCl_3$-CCl_4 or $CDCl_3$-Ac-d_6 with variable composition. Effective static relative dielectric permittivity of solution was changed from 4.3 to 5.62 by varying the composition of the mixed solvent which led to redistribution of intensities between the two sets of signals. The authors considered the two sets of signals to be originating from 'free' and ion paired species. The subsequent study by the same group on RmimTFSI in $CDCl_3$ by means of calorimetric and NMR diffusion measurements[87] revealed that the two kinds of species distinguished in the NMR spectrum are rather ion pairs and larger aggregates than ion pairs and 'free' ions as it was initially assumed. Two-sets of signal were also observed for solutions of $BmimBF_4$ in low polar solvent dioxane ($\varepsilon = 2.22$).[70]

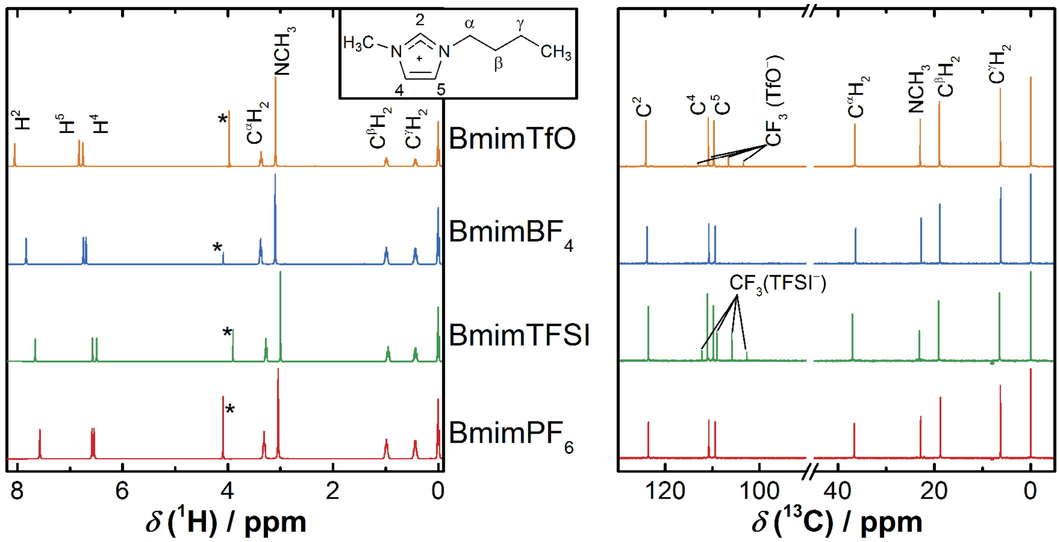

Figure 2. ^{1}H (left panel) and ^{13}C (right panel) NMR spectra of neat ILs referenced to the signal of the terminal CH_3 of cation's butyl chain (0 ppm). Residual HDO signal from the insert is marked with asterisk in the ^{1}H NMR spectra.

From the NMR spectra of neat ILs shown in Figure 2 it is apparent that the main differences in chemical shifts when referenced with respect to the terminal methyl group are observed for the imidazolium ring CH signals both for ^{1}H and ^{13}C nuclei. The effect is particularly pronounced for the C^2H^2 site. The relative order of thus referenced chemical shifts for the imidazolium ring signals is BmimTfO > $BmimBF_4$ > BmimTFSI > $BmimPF_6$. This can be considered as a first hint of the relative strength of the interionic hydrogen bonds in the neat ILs. One can also notice that the signals of the alkyl groups essentially do not depend on the nature of the anion at least in the present set of neat ILs. Another noticeable point is the scattering of the HDO signal in ^{1}H NMR signal by 0.2 ppm between the different ILs employed. This is an illustration of the extent of magnetic susceptibility variation between the studied ILs if one assumes the constancy of real chemical shift of the terminal methyl group which is questionable.[76]

A complementary confirmation of the similarity of the microenvironments for the alkyl groups and the differentiating impact of the anions on the imidazolium ring hydrogens can be gained from the IR spectra of neat ILs presented in Figure 3. Indeed, both bandshape and position of the alkyl C-H stretching vibrations observed in the range 2800-3000 cm^{-1} hardly differ between the studied ILs.

In contrast, in the region of the imidazolium ring C-H stretches (3050-3250 cm^{-1}) the entire spectral profile undergoes a redshift in the order BmimPF$_6$ > BmimTFSI ≈ BmimBF$_4$ > BmimTfO. The effect is particularly pronounced for the lowest frequency component associated with the C^2-H stretching in accordance with the relative hydrogen bond strength suggested from the NMR spectra discussed above.[20] Moreover, the bandshape of the low-frequency part of this profile is substantially different between BmimTfO and BmimTFSI on one side and BmimBF$_4$ and BmimPF$_6$ on the other side. For the former (ILs with large anions of low symmetry) the C^2-H related contribution is much stronger and appears as a distinct shoulder in the profile. This finding is an indication of particular preferential hydrogen bonding at the H^2 site in the case of BmimTfO and BmimTFSI.

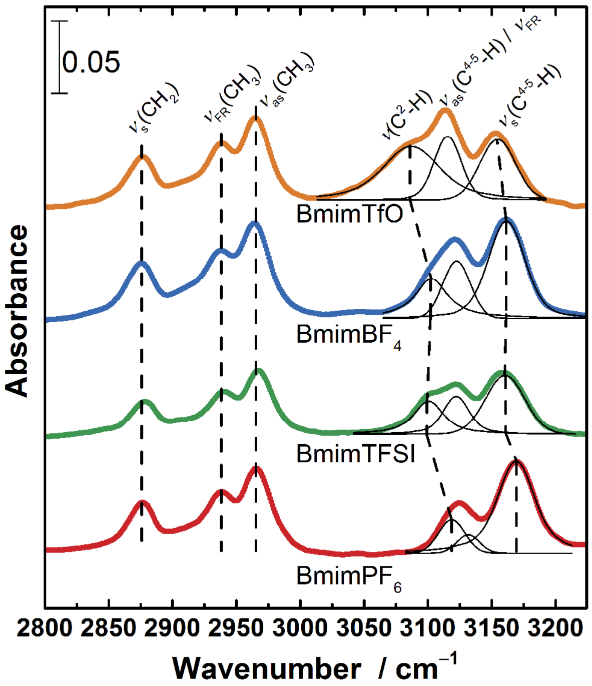

Figure 3. ATR-IR spectra of the neat ILs in the region of C-H stretching vibrations. Solid black lines are fitted individual Voigt-type profiles of the region of the imidazolium ring C-H stretches (above 3050 cm^{-1}). Dashed black lines are guides to the eye. Band assignments are taken from the literature.[20, 88]

The relative chemical shift variations in ^{1}H-NMR spectra of mixtures of BmimBF$_4$, BmimPF$_6$, BmimTfO, BmimTFSI with AN referenced to the chemical shift of terminal methyl group of cation's butyl chain as a function of IL mole fraction x_{IL} are shown in Figure 4. Our data on BmimBF$_4$-AN system agrees very well with the recently published results of Zheng *et. al.*[48] In AN all the relative chemical shift variations of the hydrogen atoms in the studied set of systems are negative. This implies that the effect of ion dissociation accompanied with the rupture of interionic hydrogen bonds overwhelms the specific solvation effects. This is not surprising since AN is only moderately polar donating.[89] Solvation of dialkylimidazolium ILs in polar aprotic solvents including AN has been studied previously from the point of view of translational and rotational dynamics by means of NMR-diffusometry[13] and dielectric relaxation spectroscopy (DRS),[12, 90] respectively. Both approaches revealed poor sensitivity of the solvation pattern to the anion and to the alkyl chain length of the cation. This was treated as a signature of cation solvation localized at the imidazolium ring.[12, 13, 90] A certain degree of IL ion association in AN was also noted concomitant with conductivity measurements.[7]

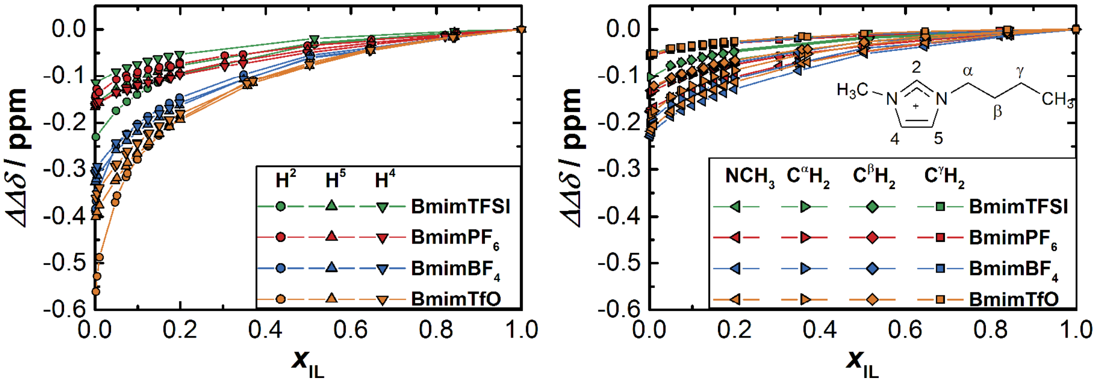

Figure 4. Relative ^{1}H chemical shift variation in mixtures of imidazolium ILs with AN. Left panel shows the values for the imidazolium ring hydrogen atoms $H^{2/4/5}$ and the values for the alkyl hydrogen atoms are presented in the right panel.

The most significant effects are observed for the imidazolium ring hydrogen atoms, particularly at high dilutions. As discussed in the previous subsection, this finding can be connected to the fact that interionic hydrogen bonds with the alkyl hydrogen atoms are rather weak compared to that with the imidazolium ring hydrogen atoms. $BmimBF_4$ and BmimTfO show the largest negative values, that is a clear indication of the interionic hydrogen bond rupture in these systems.

For a given IL, the H^2 hydrogen atom revealed to be the most sensitive one among the imidazolium ring hydrogen atoms (this is especially well pronounced for BmimTfO and BmimTFSI). Particular sensitivity of the H^2 site was noticed in most of the mentioned above studies and was related to the higher positive charge and acidity of the C^2-H^2 fragment compared to the C^4-H^4 and C^5-H^5 fragments and, hence, to the higher strength of the corresponding hydrogen bonds.[54, 74] The fact that this enhanced sensitivity of the H^2 chemical shift is much less pronounced for $BmimBF_4$ and $BmimPF_6$ also agrees with the literature data on systems containing these ILs where the difference in relative chemical shift variations between the H^2 and H^{4-5} signals did not exceed 0.1 ppm at highest dilution.[26, 27, 32, 48, 67, 75, 77-79, 91] At the same time, for mixtures containing imidazolium ILs with anions of low symmetry ($TFSI^-$, TfO^-, RSO_3^-, RCO_2^-) H^2 was found to be exceptionally sensitive just as in the present study.[16, 25, 41, 42, 54, 55, 63, 64, 66] This can be related to differences in strengths of the hydrogen bonds present in ion aggregates at H^2 and H^{4-5} sites for different ILs as it was noted in our recent paper.[92]

A notable effect is also observed for $C^{\alpha}H_2$ and NCH_3 protons (which are adjacent to the imidazolium ring) and even for $C^{\beta}H_2$. This agrees well with the results of multiple model calculations[20, 92-94] that in the most stable arrangement of the ion pairs and ion aggregates the multiatomic anions are located above the C^2-H^2 fragment which allows them to form hydrogen bonds with the adjacent alkyl hydrogen atoms of the $Bmim^+$ cation. These hydrogen bonds are considerably weaker than those with the imidazolium ring hydrogen atoms. Recently, an additional experimental confirmation of significance of these interactions in the IL liquid phase has been obtained in an isotopic substitution NMR study on neat $BmimBF_4$ and $BmimPF_6$.[95]

In the studied set of IL mixtures with AN the magnitude of relative chemical shift variations of the imidazolium ring hydrogen atoms follows$TfO^- \geq BF_4^- > PF_6^- \sim TFSI^-$. The difference between the ILs for the relative chemical shift variations of the alkyl hydrogen atoms is much more difficult to be discerned but also agrees with the proposed trend. This sequence correlates rather well with the relative hydrogen bond strengths revealed by our quantum chemical calculations[92] than with the estimated in vacuum interaction energies.[96] Relative tendency to ion-pairing as estimated with the help of thermodynamic constants of ion association derived from accurate conductivity measurements of the corresponding dilute solutions of BmimX ILs in AN[7, 90] fits the trend much better. The values of $K_A^{298.15}$ in $dm^3\ mol^{-1}$ are 24.0[7] for BmimTfO, 18.15[7] or 15.7[90] for $BmimBF_4$, 15.6[90] for $BmimPF_6$, 12.67[90] for HexmimTFSI (for BmimTFSI there is no literature data but it is expected to be higher by *ca.* 0.1-0.2 $dm^3\ mol^{-1}$). Other reported values of the association constant of these ILs in AN seem to be much less accurate and less credible: 27.0 $dm^3\ mol^{-1}$for $BmimPF_6$,[97] *ca.* 700 $dm^3\ mol^{-1}$ for $BmimBF_4$ and $BmimPF_6$,[98] 205±20 $dm^3\ mol^{-1}$ for BmimTFSI and 46±7 $dm^3\ mol^{-1}$ for BmimTfO.[99]

An observation that the difference between the ILs becomes more pronounced with dilution and even shows some enhancement at the lowest employed concentrations ($x_{IL} < 0.05$) serves as an additional hint that it is in this concentration range where the ultimate disruption of ion associates down to the individual ions takes place.[3, 17]

In contrast to ^{1}H-NMR discussed above, studies on the concentration induced variations of ^{13}C-NMR chemical shifts in mixtures of imidazolium ILs with molecular solvents are rather scarce.[27, 30, 31, 38, 55] Since ^{13}C-NMR goes as a supplement to more elaborated ^{1}H-NMR investigation, the comments are usually limited to general statements that carbon shifts roughly follow the trends established for hydrogen atoms, which is not always true though.[27, 38] Indeed, interpretation of the variations in ^{13}C chemical shifts is not that straight forward since they are not involved explicitly in the intermolecular interactions even though the observed variations are close in magnitude to those found for ^{1}H chemical shifts.[27, 30, 31, 38, 55] Another difficulty in the interpretation of the ^{13}C chemical shift variations for carbon nuclei is that the changes in microenvironment of the carbon atoms stem from both hydrogen bonding effects at the adjacent hydrogen atoms and from the electron density redistribution along the skeleton of Rmim$^+$ cation.[28] As the observed chemical shift change reflects only the net effect of electron density gain/loss at a given atom, it is rather challenging to track all the pathways of electron density redistribution and to assign it to distinct intermolecular interactions. An additional insight can be gained from the analysis of electron density distribution by means of quantum chemical calculations of representative systems.[92]

Figure 5 shows the relative ^{13}C chemical shift variations in mixtures of the studied ILs with AN. Apparently, they do not follow the patterns observed for the corresponding ^{1}H relative chemical shift variations. One can see from Figure 5 that most of the carbon atoms show positive or essentially zero $\Delta\Delta\delta\ (x)$ values, whereas the C^2 carbon for all the studied ILs and C^4, C$^\alpha$, C$^\beta$, C$^\gamma$ of BmimTFSI show negative values. Between the alkyl carbons of a given IL the effect is most pronounced for the ones adjacent to the imidazolium ring (NCH$_3$ and C$^\alpha$).

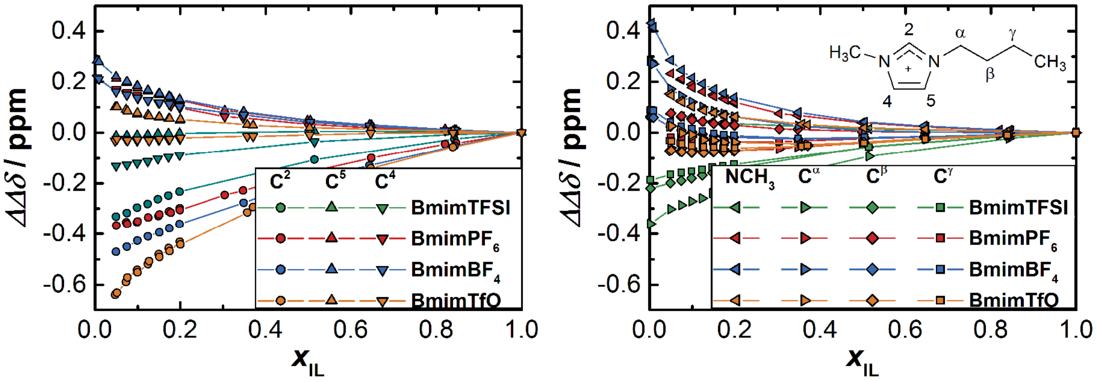

Figure 5. Relative ^{13}C chemical shift variation in mixtures of imidazolium IL with AN. Left panel shows the values for the imidazolium ring carbons C$^{2/4/5}$ and the values for the alkyl carbons are presented on the right panel.

The observed effective deshielding of most of the carbon atoms (as referenced to the terminal methyl one, $\Delta\Delta\delta\ (x) > 0$) is essentially opposite to what has been established for the corresponding hydrogen atoms. At the same time the C^2 carbon behaves in accordance with the adjacent H^2 hydrogen (Figure 4) and reveals almost the same trend in the magnitudes of the relative chemical shift variation (TfO$^-$ > BF$_4^-$ > TFSI$^-$ ~ PF$_6^-$).

Particular behavior of the relative chemical shift of this carbon atom can be related to the results of accurate analysis of electron density distribution in model representative structures.[83, 92, 93] In contrast to other carbon atoms, C^2 explicitly interacts with anion which is preferentially located on top of the C^2-H^2 fragment and the strength of this interaction is quite similar to that with the H^2 hydrogen atom. As for the other imidazolium ring carbons and the alkyl ones, these relative chemical shift variations presumably result from rather complex effects of electron density redistribution.

^{13}C relative chemical shift variations of anions in mixtures containing BmimTfO and BmimTFSI

Anions of BmimTfO and BmimTFSI ILs contain carbon atoms which allowed us to follow their ^{13}C chemical shifts in the framework of the relative chemical shift variations, *i.e.*, referenced to the terminal carbon of cation's butyl chain. Previously, an effective deshielding of the carbon atoms of the anions of RmimTFSI (when referenced to the terminal alkyl one) was observed for EmimTFSI upon heating[100] and for DodecmimTFSI upon dilution in C_6H_6.[31] In a recent study on EmimTFSI in DMSO and AN the relative chemical shift of TFSI$^-$ carbons was found to be negative upon dilution, however, the real chemical shift variation of the reference terminal carbon was unusually highly positive and the real chemical shift variation of TFSI$^-$ carbons was indicative of its deshielding upon dilution.[28] This was attributed to the effect of electron density redistribution upon loosening of the interionic interactions. Nothing was found in the literature on ^{13}C NMR chemical shift variations with concentration in RmimTfO-based systems.

Figure 6 shows the relative chemical shift variations of the carbon atoms of anions in mixtures of BmimTfO and BmimTFSI with AN. One can see that carbon atoms of the trifluoromethyl groups CF_3 behave differently in these ionic liquids: an apparent deshielding is observed for BmimTfO, while for BmimTFSI the relative chemical shift values are negative, which reflects effective shielding of the corresponding carbon atoms upon dilution in AN.

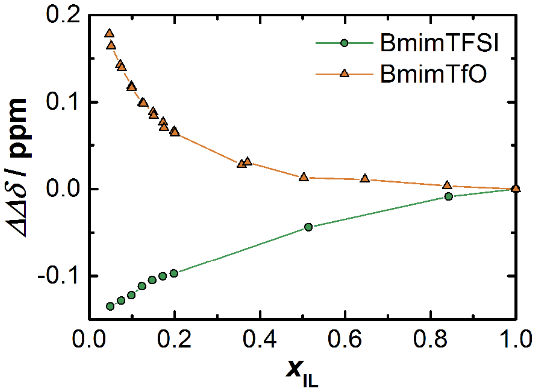

Figure 6. Relative ^{13}C chemical shift variation for CF_3 carbon atoms of anions in mixtures of BmimTfO and BmimTFSI with AN.

This difference between the two anions can be rationalized as follows. As it has been established in our recent paper[92] devoted to quantum-chemical calculations of the representative model molecular clusters, ion pair structure of BmimTfO is much more persistent than that of BmimTFSI. This is an indication of the relative stability of the ion pairs of these ILs which is also supported by the higher values of association constant estimated from low-concentration conductivity measurements.[7, 90] As a result, the main effect in solvation of BmimTFSI ion pair is the weakening of interionic interactions due to structural distortion and increased separation (this reduces Coulomb attraction and weakens non-covalent interactions, *e.g.*, interionic hydrogen bonds). The effect of charge redistribution, which is, in fact, monitored by the relative chemical shift variation, is that for BmimTFSI electron density relaxes towards it unperturbed state which is accompanied with the decrease of charge of the corresponding carbon atoms, while for BmimTfO, strengthening of the interactions with the anion, including solvation effects, leads to its polarization enhancement which is manifested in the increase of the charge of the carbon atom.

^{13}C relative chemical shift variations of AN in mixtures

The electron density redistribution in the solvent molecules can be monitored via its ^{13}C relative chemical shift variation shown in Figure 7. Here, the methyl carbon of the AN molecule was taken as a reference. In all the studied ILs the $\Delta\Delta\delta$ (x) for the ^{13}C chemical shifts of AN nitrile carbon atoms are positive with a pronounced rise at low IL content. This indicates a progressive polarization of the C-C bond in AN mainly due to polarization of the C≡N group as a result of specific solvation interactions mentioned above. The effect is more pronounced for ILs with anions having symmetric charge distribution, $BmimBF_4$ and $BmimPF_6$, than for those having the asymmetric one, BmimTfO and BmimTFSI. This may be indicative of different interaction patterns of AN molecules with anions of different spatial charge distribution. Slightly higher values observed for BmimTfO with respect to BmimTFSI may be related to the issue of TfO^- specific solvation. The exact nature of the underlying electronic effects is still to be addressed by means of theoretical methods.

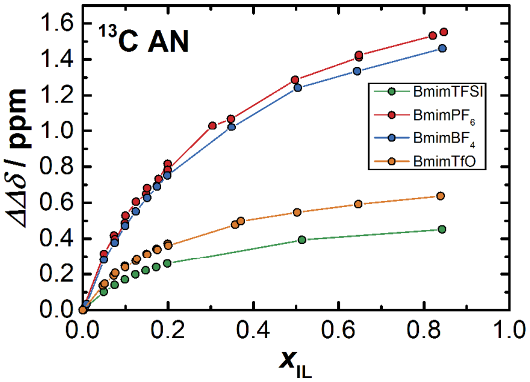

Figure 7. Relative ^{13}C chemical shift variation for CN carbons of AN molecules referenced

Conclusions

Chemical shift variation in mixture of imidazolium ILs with polar molecular solvents can be used to follow the balance between interionic and ion-solvent interactions. An approach based on referencing ^{1}H and ^{13}C NMR chemical shifts in the studied mixtures to the signal of terminal methyl of cation's butyl chain in the neat ILs is proposed. The variations in thus introduced relative chemical shifts as a function of mixture composition and the nature of its constituents are interpreted in terms of specific and non-specific intermolecular interactions.

Mixtures of four imidazolium ILs ($BmimBF_4$, $BmimPF_6$, BmimTfO, and BmimTFSI) with AN were studied over the entire range of concentrations within the proposed framework. BmimTfO and $BmimBF_4$ ILs were found to establish interionic hydrogen bonds involving the imidazolium ring hydrogen atoms and the hydrogen atoms of the adjacent alkyl groups, which are stronger than in the case of $BmimPF_6$ and BmimTFSI. Upon dilution in AN, these hydrogen bonds are progressively disrupted as a result of weakening of interionic interactions and ion dissociation which is particularly pronounced at high dilutions ($x_{IL} < 0.1$). For BmimTfO and BmimTFSI ILs, the interionic hydrogen bond with the imidazolium ring hydrogen atom H^2 was revealed to be substantially stronger than with the hydrogen atoms at positions 4-5. The relative strengths of hydrogen bonding between the imidazolium ring hydrogen atoms of cations and electronegative atoms of anions correlate well with the results from IR spectra and recent quantum-chemical calculations ($BmimTfO > BmimBF_4 \geq BmimTFSI \geq BmimPF_6$).

Solvation of the ILs in AN is not accompanied by formation of hydrogen bonds solvent-cation of an appreciable strength. The solvation of anions was investigated for BmimTfO and BmimTFSI ILs by following the ^{13}C relative chemical shifts of the corresponding CF_3 groups. $TFSI^-$ is considered to experience only the nonspecific effects of weakening of interionic interactions upon dilution while in case of BmimTfO, due to its higher propensity to ion association compared to BmimTFSI, solvent molecules interact not only with the cation but also with the anion.

Acknowledgements

BAM is thankful to the French Government and CAMPUS FRANCE agency for financial support.

References

1. M. Smiglak, J. M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D. R. MacFarlane and R. D. Rogers, *Chem. Commun.*, 2014, **50**, 9228-9250.
2. R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792-793.
3. H. K. Stassen, R. Ludwig, A. Wulf and J. Dupont, *Chem. – Eur. J.*, 2015, **21**, 8324-8355.
4. A. M. Rizzuto, R. L. Pennington and K. D. Sienerth, *Electrochim. Acta*, 2011, **56**, 5003-5009.
5. S. Trivedi, A. Sarkar and S. Pandey, *Chem. Eng. J.*, 2009, **147**, 36-42.
6. A. Chagnes, M. Diaw, B. Carré, P. Willmann and D. Lemordant, *J. Power Sources*, 2005, **145**, 82-88.
7. O. N. Kalugin, I. V. Voroshylova, A. V. Riabchunova, E. V. Lukinova and V. V. Chaban, *Electrochim. Acta*, 2013, **105**, 188-199.
8. V. V. Chaban, I. V. Voroshylova, O. N. Kalugin and O. V. Prezhdo, *J. Phys. Chem. B*, 2012, **116**, 7719-7727.
9. I. V. Voroshylova, S. R. Smaga, E. V. Lukinova, V. V. Chaban and O. N. Kalugin, *J. Mol. Liq.*, 2015, **203**, 7-15.
10. E. Couadou, J. Jacquemin, H. Galiano, C. Hardacre and M. Anouti, *J. Phys. Chem. B*, 2013, **117**, 1389-1402.
11. T. Sonnleitner, D. A. Turton, S. Waselikowski, J. Hunger, A. Stoppa, M. Walther, K. Wynne and R. Buchner, *J. Mol. Liq.*, 2014, **192**, 19-25.
12. A. Stoppa, J. Hunger, G. Hefter and R. Buchner, *J. Phys. Chem. B*, 2012, **116**, 7509-7521.
13. B. A. Marekha, O. N. Kalugin, M. Bria, R. Buchner and A. Idrissi, *J. Phys. Chem. B*, 2014, **118**, 5509–5517.
14. W.-Y. Hsu, C.-C. Tai, W.-L. Su, C.-H. Chang, S.-P. Wang and I. W. Sun, *Inorg. Chim. Acta*, 2008, **361**, 1281-1290.
15. A. Radhi, K. A. Le, M. E. Ries and T. Budtova, *J. Phys. Chem. B*, 2015, **119**, 1633-1640.
16. C. A. Hall, K. A. Le, C. Rudaz, A. Radhi, C. S. Lovell, R. A. Damion, T. Budtova and M. E. Ries, *J. Phys. Chem. B*, 2012, **116**, 12810-12818.
17. J. Dupont, *J. Braz. Chem. Soc.*, 2004, **15**, 341-350.
18. A. Bagno, F. Rastrelli and G. Saielli, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2005, **47**, 41-93.
19. Y. Marcus and G. Hefter, *Chem. Rev.*, 2006, **106**, 4585-4621.
20. B. A. Marekha, V. A. Koverga, M. Moreau, M. Kiselev, T. Takamuku, O. N. Kalugin and A. Idrissi, *J. Raman Spectrosc.*, 2015, **46**, 339-352.
21. J. S. Wilkes, J. A. Levisky, J. L. Pflug, C. L. Hussey and T. B. Scheffler, *Anal. Chem.*, 1982, **54**, 2378-2379.
22. J. S. Wilkes, J. S. Frye and G. F. Reynolds, *Inorg. Chem.*, 1983, **22**, 3870-3872.
23. A. A. Fannin, L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.*, 1984, **88**, 2609-2614.
24. A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, 1994, 3405-3413.
25. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
26. B.-M. Su, S. Zhang and Z. C. Zhang, *J. Phys. Chem. B*, 2004, **108**, 19510-19517.
27. C. Zhai, J. Wang, Y. Zhao, J. Tang and H. Wang, *Z. Phys. Chem.*, 2006, **220**, 775-785.
28. T. Takamuku, H. Hoke, A. Idrissi, B. A. Marekha, M. Moreau, Y. Honda, T. Umecky and T. Shimomura, *Phys. Chem. Chem. Phys.*, 2014, **16**, 23627-23638.
29. N. Dias, K. Shimizu, P. Morgado, E. J. M. Filipe, J. N. Canongia Lopes and F. Vaca Chávez, *J. Phys. Chem. B*, 2014, **118**, 5772-5780.

30. T. Shimomura, S. Inoue, S. Kadohata, T. Umecky and T. Takamuku, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20565-20576.
31. T. Shimomura, T. Takamuku and T. Yamaguchi, *J. Phys. Chem. B*, 2011, **115**, 8518-8527.
32. F. D'Anna, M. Cascino, P. Lo Meo, S. Riela and R. Noto, *ARKIVOC*, 2009, **2009**, 30-46.
33. K. R. Seddon, A. Stark and M.-J. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275-2287.
34. J. Dupont, P. A. Z. Suarez, R. F. De Souza, R. A. Burrow and J.-P. Kintzinger, *Chem. – Eur. J.*, 2000, **6**, 2377-2381.
35. C. S. Consorti, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, D. H. Farrar, A. J. Lough, W. Loh, L. H. M. da Silva and J. Dupont, *J. Phys. Chem. B*, 2005, **109**, 4341-4349.
36. C.-P. Zhai, X.-J. Liu, Y. Zhao and J.-J. Wang, *Acta Phys.-Chim. Sin.*, 2009, **25**, 1185-1189.
37. J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133-2140.
38. Z. Cui-ping, W. Jian-ji, X. Xiao-peng, W. Han-qing and C. Miao, *Chin. J. Chem. Phys.*, 2006, **19**, 447.
39. C. Zhai, J. Wang, Y. Zhao and J. Tang, *Z. Anorg. Allg. Chem.*, 2009, **223**, 839-847.
40. Q.-G. Zhang, N.-N. Wang and Z.-W. Yu, *J. Phys. Chem. B*, 2010, **114**, 4747-4754.
41. Q.-G. Zhang, N.-N. Wang, S.-L. Wang and Z.-W. Yu, *J. Phys. Chem. B*, 2011, **115**, 11127-11136.
42. E. Ruiz, V. R. Ferro, J. Palomar, J. Ortega and J. J. Rodriguez, *J. Phys. Chem. B*, 2013, **117**, 7388-7398.
43. R. Lungwitz and S. Spange, *New J. Chem.*, 2008, **32**, 392-394.
44. R. Lungwitz and S. Spange, *ChemPhysChem*, 2012, **13**, 1910-1916.
45. S. Hesse-Ertelt, T. Heinze, B. Kosan, K. Schwikal and F. Meister, *Macromol. Symp.*, 2010, **294**, 75-89.
46. A. Lyčka, R. Doleček, P. Šimûnek and V. Macháček, *Magn. Reson. Chem.*, 2006, **44**, 521-523.
47. V. Balevicius, Z. Gdaniec, K. Aidas and J. Tamuliene, *J. Phys. Chem. A*, 2010, **114**, 5365-5371.
48. Y.-Z. Zheng, N.-N. Wang, J.-J. Luo, Y. Zhou and Z.-W. Yu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 18055-18064.
49. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795-1818.
50. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffmann and K. W. Zilm, *Pure Appl. Chem.*, 2008, **80**, 59-84.
51. T. Umecky, T. Takamuku, T. Matsumoto, E. Kawai, M. Takagi and T. Funazukuri, *J. Phys. Chem. B*, 2013, **117**, 16219-16226.
52. T. Takamuku, private communication. For certain mixtures IL+solvent the observed concentration trend of chemical shifts changes its direction after correction for bulk magnetic susceptibility. It is thus evident that the magnitude of the correction can be at least on the order of tens of ppm.
53. J. Wang, H. Yao, Y. Nie, X. Zhang and J. Li, *J. Mol. Liq.*, 2012, **169**, 152-155.
54. T. Takamuku, Y. Honda, K. Fujii and S. Kittaka, *Anal. Sci.*, 2008, **24**, 1285-1290.
55. T. Shimomura, K. Fujii and T. Takamuku, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12316-12324.
56. T. Takamuku, T. Shimomura, K. Sadakane, M. Koga and H. Seto, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11070-11080.
57. K. Mizuno, Y. Tamiya and M. Mekata, *Pure Appl. Chem.*, 2004, **76**, 105-114.
58. K. Momoki and Y. Fukazawa, *Anal. Chem.*, 1990, **62**, 1665-1671.
59. K. Momoki and Y. Fukazawa, *Anal. Sci.*, 1994, **10**, 53-58.
60. L. N. Mulay and M. Haverbusch, *Rev. Sci. Instrum.*, 1964, **35**, 756-757.
61. A. Stoppa, J. Hunger and R. Buchner, *J. Chem. Eng. Data*, 2009, **54**, 472-479.
62. L. Yangzhong, NMR Temperature Calibration, http://staff.ustc.edu.cn/~liuyz/methods/NMR_VT_calibration.htm, (accessed Aug 03, 2014).

63. J. W. Russo and M. M. Hoffmann, *J. Chem. Eng. Data*, 2011, **56**, 3703-3710.
64. A. Stark, A. W. Zidell and M. M. Hoffmann, *J. Mol. Liq.*, 2011, **160**, 166-179.
65. N. T. Scharf, A. Stark and M. M. Hoffmann, *J. Phys. Chem. B*, 2012, **116**, 11488-11497.
66. A. Stark, A. W. Zidell, J. W. Russo and M. M. Hoffmann, *J. Chem. Eng. Data*, 2012, **57**, 3330-3339.
67. Y. Xu, Y. Gao, L. Zhang, J. Yao, C. Wang and H. Li, *Sci. China Chem.*, 2010, **53**, 1561-1565.
68. M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo and A. Lopes, *Green Chem.*, 2007, **9**, 481-490.
69. R. C. Remsing, Z. Liu, I. Sergeyev and G. Moyna, *J. Phys. Chem. B*, 2008, **112**, 7363-7369.
70. F. D'Anna, V. Frenna, S. La Marca, R. Noto, V. Pace and D. Spinelli, *Tetrahedron*, 2008, **64**, 672-680.
71. T. Gutel, C. C. Santini, A. l. A. H. Pádua, B. Fenet, Y. Chauvin, J. N. Canongia Lopes, F. o. Bayard, M. F. Costa Gomes and A. S. Pensado, *J. Phys. Chem. B*, 2009, **113**, 170-177.
72. R. Vreekamp, D. Castellano, J. Palomar, J. Ortega, F. Espiau, L. s. Fernández and E. Penco, *J. Phys. Chem. B*, 2011, **115**, 8763-8774.
73. F. D'Anna, S. Marullo, P. Vitale and R. Noto, *ChemPhysChem*, 2012, **13**, 1877-1884.
74. F. Cesare Marincola, C. Piras, O. Russina, L. Gontrani, G. Saba and A. Lai, *ChemPhysChem*, 2012, **13**, 1339-1346.
75. T. Singh and A. Kumar, *J. Phys. Chem. B*, 2007, **111**, 7843-7851.
76. S. Cha, M. Ao, W. Sung, B. Moon, B. Ahlstrom, P. Johansson, Y. Ouchi and D. Kim, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9591-9601.
77. M. Moreno, F. Castiglione, A. Mele, C. Pasqui and G. Raos, *J. Phys. Chem. B*, 2008, **112**, 7826-7836.
78. H. Abe, N. Hatano, Y. Ima, S. Ohta, A. Shimizu and Y. Yoshimura, *Open J. Phys. Chem.*, 2011, **1**, 70-76.
79. T. Singh, K. S. Rao and A. Kumar, *ChemPhysChem*, 2011, **12**, 836-845.
80. S. A. Katsyuba, T. P. Griaznova, A. Vidiš and P. J. Dyson, *J. Phys. Chem. B*, 2009, **113**, 5046-5051.
81. S. Tsuzuki, H. Tokuda and M. Mikami, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4780-4784.
82. K. Dong, Y. Song, X. Liu, W. Cheng, X. Yao and S. Zhang, *J. Phys. Chem. B*, 2012, **116**, 1007-1017.
83. P. A. Hunt, C. R. Ashworth and R. P. Matthews, *Chem. Soc. Rev.*, 2015, **44**, 1257-1288.
84. G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory*, Oxford University Press, 2009.
85. R. G. Bryant, *J. Chem. Educ.*, 1983, **60**, 933.
86. J. D. Tubbs and M. M. Hoffmann, *J. Solution Chem.*, 2004, **33**, 381-394.
87. N. Scharf, A. Stark and M. Hoffmann, *J. Solution Chem.*, 2013, **42**, 2034-2056.
88. Y. Jeon, J. Sung, C. Seo, H. Lim, H. Cheong, M. Kang, B. Moon, Y. Ouchi and D. Kim, *J. Phys. Chem. B*, 2008, **112**, 4735-4740.
89. C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Fourth, Updated and Enlarged Edition edn., 2011.
90. M. Bešter-Rogač, A. Stoppa and R. Buchner, *J. Phys. Chem. B*, 2014, **118**, 1426-1435.
91. T. Singh and A. Kumar, *Vib. Spectrosc.*, 2011, **55**, 119-125.
92. B. A. Marekha, O. N. Kalugin and A. Idrissi, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16846-16857.
93. R. P. Matthews, C. Ashworth, W. Tom and A. H. Patricia, *J. Phys.: Condens. Matter*, 2014, **26**, 284112.
94. Y. Danten, M. I. Cabaço and M. Besnard, *J. Mol. Liq.*, 2010, **153**, 57-66.
95. A. Khrizman, H. Y. Cheng, G. Bottini and G. Moyna, *Chem. Commun.*, 2015, **51**, 3193-3195.

96. S. Tsuzuki, H. Tokuda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 16474-16481.
97. R. Jan, G. Rather and M. Bhat, *J. Solution Chem.*, 2013, **42**, 738-745.
98. H. Wang, J. Wang, S. Zhang, Y. Pei and K. Zhuo, *ChemPhysChem*, 2009, **10**, 2516-2523.
99. A. V. Belov and S. N. Solov'ev, *Russ. J. Phys. Chem.*, 2014, **88**, 1351-1356.
100. K. Fujii, Y. Soejima, Y. Kyoshoin, S. Fukuda, R. Kanzaki, Y. Umebayashi, T. Yamaguchi, S.-i. Ishiguro and T. Takamuku, *J. Phys. Chem. B*, 2008, **112**, 4329-4336.