¹H, ¹³C NMR and DFT Study of Hydrogen Bonding in Imidazolium-based Ionic Liquids

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Abstract

The ionic liquid 1-decyl-3-methyl-imidazolium bromide [C_{10}mim][Br], the neat material, and also dissolved (~0.01 mole fraction) in various dielectric media (acetonitrile, benzene, chloroform, dichloromethane, methanol, 2-butanol and H_2O) was studied using ¹H and ¹³C NMR spectroscopy. The most important interaction in this compound is considered to be the Br^-...H–$C2^+$ hydrogen bond, which is formed between the anions and cations. The obtained results show that dielectric medium influence mostly the behavior of the Br^-...H–$C2^+$ bridge proton. The changes observed in ¹H and ¹³C NMR spectra of [C_{10}mim][Br] with increasing solvents polarity and temperature can be explained applying the model of the lengthening of the H2...Br^- bond with the accompanying thickening of the solvation shell of bromine anion and C2–H bond contraction. The short-range order effects related to the configuration of neighboring dipoles of solvent molecules are more important for the solvation ability of small anions than the bulk solvent field effect. However, the solvents, molecules of which tend to associate via hydrogen bonding, can significantly affect the dynamics of anions.

Keywords: Ionic liquids; NMR spectroscopy; Hydrogen bonding.

1. Introduction

Ionic liquids (ILs), by definition, are compounds consisting entirely of ions, but in contrast to 'classical' salts they are liquid state at the room temperature or close to it.[1, 2] These systems can be considered as one of the most successful breakthroughs creating smart multifunctional materials and compositions that posse many appealing features.[3–7] Selecting combinations of anionic and cationic subsystems one can alter defined physical and chemical properties of ILs getting possibilities to sense and to control various molecular processes in these media. It makes ILs very attractive for research and technologies. And indeed, ILs have already demonstrated their unique properties in many fields of high technologies, including (bio-) catalysis, battery and fuel cells, electrochemistry, *etc*.

A physical understanding on a molecular level how the certain unique properties of ILs may arise from the long-range interionic interactions coupled with their structural features and dynamics is one of the main challenges for fundamental research. Hydrogen bonding between the anions and cations can play an extremely important role there. This was demonstrated switching off the H-bond contribution in closely related ILs by proper methylation.[8] Localized and directionally depending H-bonding disorder the Coulomb network, and the system then deviates from the charge symmetry.[8 and Refs. cited therein] This intensifies the ionic dynamics and results in a significant decrease of melting points and viscosity. Hence, some important macroscopic properties of ILs can be tuned by adjusting the ratio between Coulomb- and the H-bond contributions, even the latter being energetically less significant.

Ionic liquids are very intriguing systems to study also in respect of purely H-bonding phenomena. In many of ILs the anions are the conjugate bases of strong and very

strong acids – some halogenides (Cl⁻, Br⁻), trifluoroac-etate (CF₃COO⁻), triflate (CF₃SO₃⁻), *etc*.[9] Hence, some of ILs can be considered as ionic pair model systems formed as a result of very 'deep' proton transfer (PT) from the acid to the defined base. The cationic subsystem in such ILs consists of corresponding protonated bases. However, these ionic pairs are kind of 'inverted' in respect of the tra-ditional ones that appear in numerous H-bond systems with PT.[10] Such protonated structure can be considered as the 'ground state' that can be disturbed by various external stimuli (solvent, temperature, *etc*) reversing the system to the neutral H-bonding. Another point that makes ionic liq-uids convenient and attractive to study as model PT sys-tems is their good solubility in many traditional organic solvents (weakly polar and even non-polar).

The purpose of present work was to study the effects of solvent and temperature on H-bonding in one of imida-zolium-based room-temperature ionic liquid, namely - the 1-decyl-3-methyl-imidazolium bromide ([C₁₀mim][Br]), the neat compound as well as its solutions in acetonitrile, benzene, chloroform, dichloromethane, methanol, water, *etc* applying ¹H and ¹³C NMR spectroscopy. In order to obtain additional insight into the experimental observa-tions, the quantum chemistry DFT calculations of the electronic structure and ¹H and ¹³C magnetic shielding tensors of [C₁₀mim][Br] were performed.

2. Experimental

Commercial acetonitrile, benzene, chloroform-*d*, dichloromethane, 2-butanol, methanol (all from Aldrich, see Table 1) were purified by standard methods;[11] the wa-ter used was freshly bidistilled; the 1-decyl-3-methyl-imi-dazolium bromide ([C₁₀mim][Br], from Merck KGaA, Darmstadt) was dried under vacuum at 80 °C for one day. Its structure and atom numbering are shown in Fig.1. The samples containing [C₁₀mim][Br] in solutions (0.01 mole fractions) were prepared by weighting (± 0.1 mg) the components.

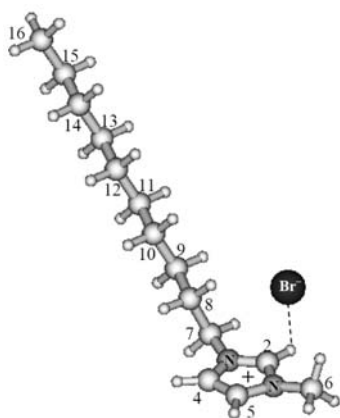**Fig. 1.** The optimized structure of [C₁₀mim][Br] (DFT B3LYP/6-31++G**, *in vacuo*).

Table 1. The used solvents and their dielectric parameters: dielec-tric constants (ε) and dipole moments (μ); the values taken from.[12]

Solvent	Abbreviation used in text	ε	μ (D)
Acetonitrile	AN	37.5	3.44
Benzene	BE	2.29	0
Chloroform-*d*	CHL	4.81	1.08
Dichloromethane	DCM	9.0	1.6
2-butanol	2BuOH	15.8	1.66
Methanol	MeOH	32.6	1.7
Water	H₂O	80.1	1.85

NMR experiments were carried out on a BRUKER AVANCE[II]/400 NMR spectrometer operating at 400 and 100 MHz for ¹H and ¹³C respectively using 5 mm BBO probe-head. The temperature in a probe was controlled with an accuracy of ± 0.5 K. The signal of DSS in D₂O so-lution in capillary insert was used as the reference and then converted in respect tetramethylsilane (TMS) taking δ(TMS) = 0.015 ppm.[12] The D₂O in the same capillary in-sert was used for locking.

3. DFT Calculations

The calculations of the magnetic shielding tensors of 1-decyl-3-metil- imidazolium bromide [C₁₀mim][Br] have been performed using the density functional theory (DFT). The applied approach was earlier checked in vari-ous cases[9, 13, 14] and found to be adequate for this purpose. It produces an excellent coincidence of calculated and ex-perimentally measured ¹H and ¹³C NMR shifts for nuclei in very strong H-bond systems,[9, 13] as well as for rather 'inert' groups, e.g. –CH₃ protons.[14]

The full geometry optimization in the ground state was performed *in vacuo* using the B3LYP functional com-bined with the 6-31++G** basis set (Fig. 1). The magnet-ic shielding tensors have also been calculated *in vacuo* ap-plying the modified hybrid functional of Perdew, Burke and Ernzerhof (PBE1PBE) with the 6-311++G(2d,2p) ba-sis set. Gaussian 03 program[15] was used for all our calcu-lations. The gauge-including atomic orbital (GIAO) ap-proach[16] was used to ensure gauge invariance of the re-sults. The calculated chemical shifts were transformed to the δ-scale as the difference between the isotropic part of magnetic shielding tensor (σ_{iso}) and that of TMS. The val-ues of isotropic part of magnetic shielding tensors of ¹³C and ¹H nuclei of the TMS were taken from.[17]

4. Results and Discussion

1-decyl-3-methyl-imidazolium bromide ([C₁₀mim] [Br], Fig.1) was chosen for the present studies for several reasons. ¹H, ¹³C and ⁸¹Br NMR spectra of [C₁₀mim][Br] have already been analyzed,[18] however, focusing mainly

on the mesoscopic heterogeneity effects in the neat IL and its solutions in various solvents. The appearance of long living nonequilibrium aggregates and micro-hetero-geneities in [C$_{10}$mim][Br]/water solution was studied using ^{1}H NMR signal shape analysis.[19] An aggregation and phase behavior of [C$_{10}$mim][Br] and similar ILs in water and alcohol solutions have been investigated using SAXS,[3] polarized optical microscopy techniques,[3, 4] IR and Raman spectroscopy[20–23] and ^{1}H NMR.[23–25] In many of their applications ILs are used as co-solvents together with other substances that can vary their properties very significantly. Therefore in the present work the special attention was put on ^{1}H and ^{13}C chemical shifts of [C$_{10}$mim][Br] in various solvents (nonpolar, weakly- and very polar, with- or without H-bond donor groups) and in a wide range of temperatures. Some of experimental and calculated spectra are presented in Figs. 2 and 3. The spectra are comparable with those for [C$_8$mim][Cl] and [C$_{12}$mim][Br] given in,[25, 26] respectively.

Fig. 3. ^{13}C NMR spectra of [C$_{10}$mim][Br]: theoretically calculated, in the neat ionic liquid and in solution in CHL; for carbons numbering see Fig. 1; the signal of CHL (at 77.36 ppm), when used as the solvent, is marked by*.

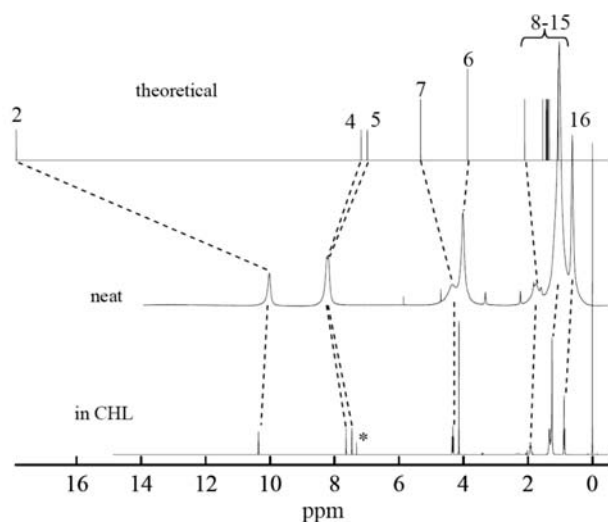**Fig. 2.** ^{1}H NMR of spectra of [C$_{10}$mim][Br]: theoretically calculated, in the neat ionic liquid and in solution in CHL; for the numbering see Fig. 1; the signal of CHL (at 7.26 ppm), when used as the solvent, is marked by*.

It is very often assumed that anions can bind to all three imidazolium ring protons of [C$_{10}$mim][Br]. However several crystallographic, NMR and DFT studies indicated that the H-bonds involving H2 proton (Fig. 1) are much stronger than those involving H4 and H4 protons.[8, 27, 28 and the Refs therein] Very nice experimental evidence was obtained from the analysis of the isotope effects on the chlorine ion $^{35/37}$Cl and ^{1}H NMR signals of [C$_4$mim][Cl] deuterated isotopologues.[28] Much stronger dependency of ^{1}H chemical shift on concentration of several imidazolium based ILs in aqueous solution observed for H2 proton than for protons H4 and H5[18, 25] can be considered as an indirect support for this statement. The strongest upfield shifts of ^{1}H and ^{13}C NMR signals of
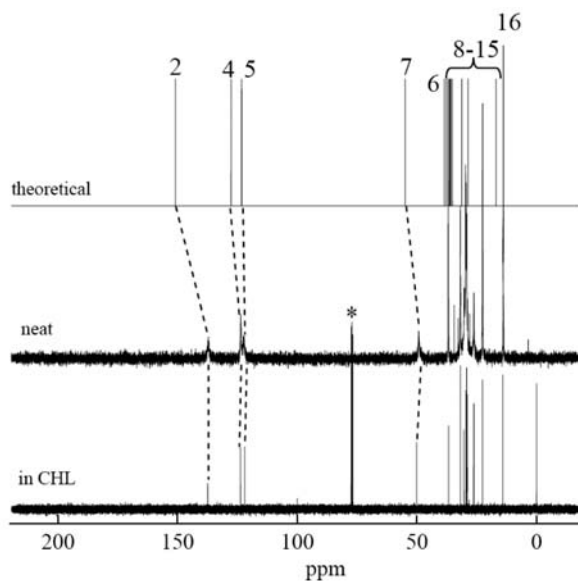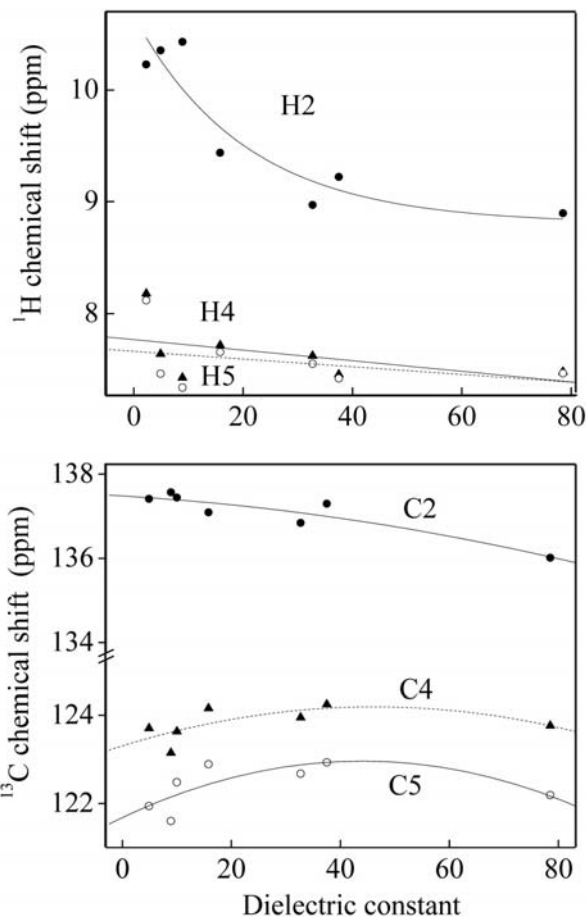

Fig. 4. Experimental dependencies of ^{1}H and ^{13}C chemical shifts of imidazolium ring nuclei on solvent dielectric constant (points - experiment, lines - fitting using regression analysis).

[C_{10}mim][Br] with increasing solvent dielectric constant (from $\varepsilon = 2.29$ (BE) to ~80 (H_2O), see Table 1) have also been determined in the present work for H2 proton and C2 carbon (Fig. 4). With increasing solvent dielectric constant the decreasing difference in magnetic shielding of H4 and H5 protons was observed with a tendency to coalescence in the most polar solvents (Fig. 4). However there are some large offsets of the experimental points from the linear regression lines at low ε. These can be due to the reasons discussed below (the presence or lack of H-bond donor groups in the solvent molecules, short-range order effects) that are not so clearly pronounced in the chemical shift *vs.* dielectric constant plot.

In order to explain these experimental observations, the quantum chemistry DFT calculations of the electronic structure and magnetic shielding tensors of [C_{10}mim][Br] were performed. All above mentioned changes in ^{1}H and ^{13}C NMR spectra with increasing ε can be reproduced applying the model of the lengthening of the H2...Br$^-$ bond and the thickening of solvation shell of bromine anion. It is symbolically presented in Fig. 5. The chemical shifts were analyzed at two single points – using complete optimized geometry (Fig. 1) with H2...Br$^-$ distance R(H2...Br$^-$) value of 2.19 Å, as well as with R(H2...Br$^-$) stretched to 5.19 Å. And indeed, the most significant effect is clearly reflected on the upfield shifts of H2 proton and C2 carbon (Fig. 6). Also the decreasing difference in magnetic shielding of H4 and H5 protons from 0.19 (optimized geometry) to 0.15 ppm (stretched H2...Br$^-$ distance) can be stated. The chemical shifts of protons and carbons in the alkyl chain are rather insensitive to the lengthening of the H2...Br$^-$ bond (Fig. 6), and this agrees with the experiment.

Another remarkable feature that elucidates the Br$^-$...H–C2$^+$ bridge in [C_{10}mim][Br] to behave quite differently from the 'traditional' H-bonds is the temperature

Fig. 6. The calculated ^{1}H and ^{13}C NMR shifts of [C_{10}mim][Br] (DFT PBE1PBE/6-311++G(2d,2p), *in vacuo*) using optimized geometry with the H2...Br$^-$distance of 2.19 Å (black columns) and with R(H2...Br$^-$) stretched to 5.19 Å. (grey columns); for the numbering see Fig. 1.
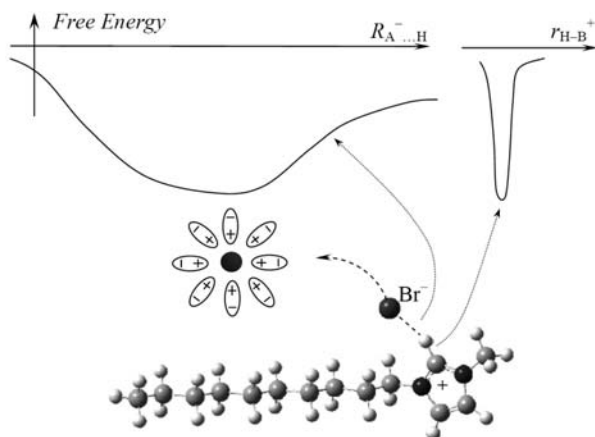

Fig. 5. The model of the lengthening of the H2...Br$^-$ distance with the accompanying thickening of solvation shell of bromine anion by solvent molecules. Note the changes in H2...Br$^-$ distance is energetically much less restricted than in H–C2$^+$.
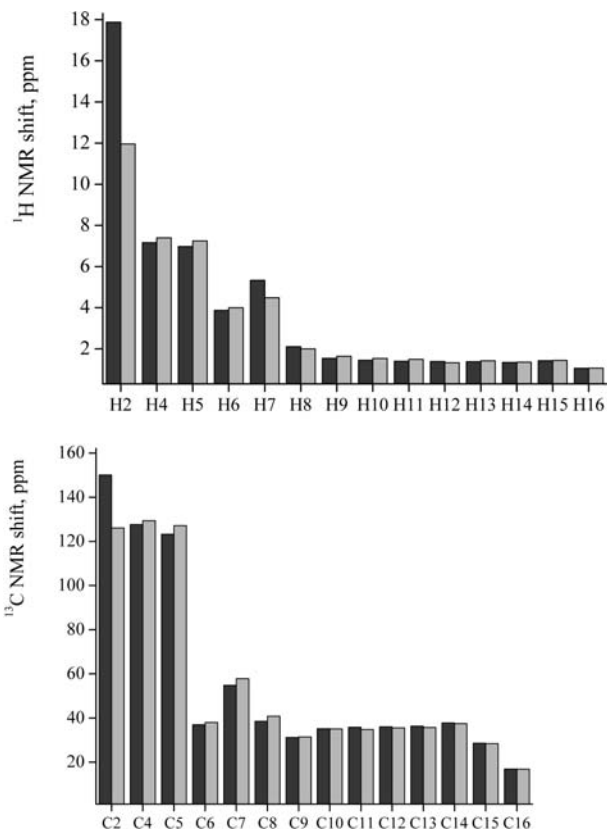
dependency of ^{1}H chemicals shifts. Very weak dependence of the chemical shift of H2 proton on temperature ($\Delta\delta/\Delta T \sim + 10^{-3}$ ppm/deg) in comparison with that for H_2O (in solution) or HDO (in D_2O capillary insert) signals ($\Delta\delta/\Delta T \sim - 10^{-2}$ ppm/deg) was observed (Fig. 7). Moreover, the slopes $\Delta\delta/\Delta T$ for the Br$^-$...H–C2$^+$ bridge and water have even the opposite signs. It can be supposed that the ions dynamics is intensified with the temperature. This motion partially destroys their solvation shells and causes the shortening of H2...Br$^-$ bond. A coalescence of ^{1}H NMR signals of H4 and H5 protons was detected, similarly to those observed at the dilution of [C_{10}mim][Br] in media of increasing polarity (Figs. 4 and 7). These observations somehow correlate with the results of FTIR studies on the other imidazolium-based ILs, where the C2–H and C4,5–H stretching bands yielding a blue-shift with increasing dilution in water have been found.[30] The data lead to suggestion that the polar media may significantly weaken the electron density and interaction between cation and anion, thereby leading to a C–H bond contraction and to corresponding changes in spectra. This and other related aspects of H-bonded systems have been extensively studied by various computational treatments.[31–33]
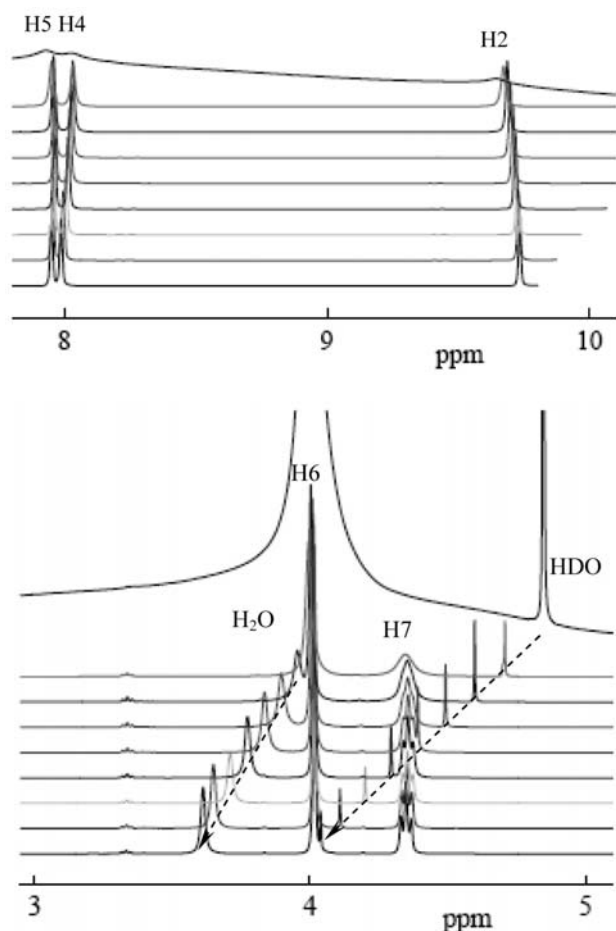
Fig. 7. Evolution of ^{1}H NMR spectrum of $[C_{10}mim][Br]$ in water (0.6 mole fraction of H_2O) with increasing temperature: 288, 300, 310, 320, 330, 340, 350, 360 and 368 K (from up to down). Note the phase transition at *ca* 290 K, most probably from the solid IL + ice to aqueous solution + hexagonal or lamellar phase.[4] More comments in text.

Some comments concerning the presence or lack of H-bond donor groups in the solvent molecules should be given when discussing the H-bonding in ILs. Analyzing the data presented in Fig. 4, *viz.* the chemical shift dependencies on dielectric constant, it seems that the presence of donor group in the solvent molecules is not crucial at all for the solvation ability. E.g. acetonitrile (AN) molecules having no H-bond donor groups solvate Br^{–} ions intermediately between alcohols and water. This is slightly in contrast with the NMR data for $[C_4mim][Cl]$ solutions in H_2O and DMSO,[29] where the relative weakness of DMSO to solvate the Cl^{–} ions was noted. However, the chemical shift dependence on the dipole moment of solvent molecules for H2 proton (Fig. 8) clearly reveals a new interesting feature. Namely, the solvents used for the experiments can be divided into two groups – having weak dipole moments and devoid of donor groups (BE, CHL, DCM) and those, which molecules show tendency to link via hydrogen bonds into the H-bond networks, and

having large dipole moments (2BuOH, MeOH, H_2O, AN, Fig. 8). Most probably, that in the culminating case of AN, as the solvent, small anions, like halogenides (Cl^{–}, Br^{–}), can be captured in the cavities of the aggregates of AN molecules build via strong dipole-dipole interactions.[14, 34] In other words it indicates that the short-range order effects related to the configuration of neighboring dipoles are more important than the bulk effect of solvent field that stronger correlates with ε values. However, the solvents, molecules of which associate via hydrogen bonding, affect the dynamic of anions more significantly than those with dipole-dipole interactions only. Very significant broadening of [81]Br NMR signal in the solutions of $[C_{10}mim][Br]$ in some of H-bond network forming solvents (5500 and 6500 Hz in methanol and H_2O, respectively) has been observed, whereas quite narrow lines (420–1300 Hz) have been registered at the same conditions in DCM and AN solutions.[18]
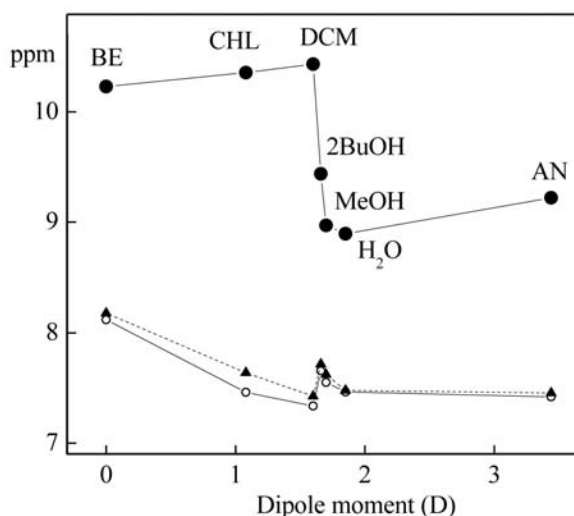

Fig. 8. Chemical shifts of [C10mim][Br] imidazolium ring protons (● - H2, ▲ - H4, ○ - H5) dependency on the dipole moment of solvent molecules.

5. Conclusions

The analysis of the solvent and temperature effects on NMR signals of IL provides new valuable information concerning interactions and structural changes in ionic liquids.

The changes observed in ^{1}H and ^{13}C NMR spectra of $[C_{10}mim][Br]$ with increasing solvents polarity and temperature can be explained applying the model of the lengthening of the H2...Br^{–} bond with the accompanying thickening of solvation shell of bromine anion and C2–H bond contraction.

The short-range order effects related to the configuration of neighboring dipoles of solvent molecules are more important for the solvation ability of small anions

than the bulk solvent field effects. However, the solvents, molecules of which tend to associate via hydrogen bonding, can significantly affect the dynamic of anions.

7. References

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Povzetek

Ionsko tekočino 1-decil-3-metil-imidazolijev bromid, [C10mim][Br], tako čisto spojino kot spojino raztopljeno v različnih dielektričnih topilih (acetonitril, benzen, kloroform, diklorometan, metanol, 2-butanol, voda; povsod molski delež ~ 0.01), smo preučevali z ^{1}H in ^{13}C NMR spektroskopijo. Najpomembnejša interakcija v tej spojini je vodikova vez Br$^-$...H–C2$^+$. Rezultati kažejo, da dielektrična topila vplivajo na vedenje protona v omenjeni vodikovi vezi. Spremembe, ki jih opazimo v ^{1}H in ^{13}C NMR spektrih [C10mim][Br] pri povečevanju polarnosti topila in pri višanju temperature, je moč pojasniti s pomočjo modela, v okviru katerega predpostavljamo, da se dolžina vezi H...Br$^-$ veča, dolžina vezi C2–H pa manjša s tem, ko se debelina plašča molekul topila okoli bromovega aniona veča. Za solvatacijsko sposobnost majhnih anionov je bolj kot povprečno polje topila pomembna konfiguracija bližnjih dipolov molekul topila. Gre torej za vpliv reda kratkega dosega. Topila, katerih molekule rade asocirajo prek vodikovih vezi, lahko znatno vplivajo na dinamiko anionov.