

# C-4. NMR SPECTROSCOPY MONITORING OF PROTON/DEUTERON EXCHANGE IN AQUEOUS SOLUTIONS OF IONIC LIQUIDS FORMING HYDROGEN BOND: A ROLE OF ANIONS, SELF-AGGREGATION, AND MESOPHASE FORMATION

Vytautas Klimavičius, Vytautas Balevičius

Department of General Physics and Spectroscopy, Vilnius University, Sauletekio 9-3, LT-10222 Vilnius, Lithuania

**Abstract.** The H/D exchange process in the imidazolium-based room temperature ionic liquids (RTILs) 1-decyl-3-methyl-imidazoliumbromide- and chloride ( $[C_{10}mim][Br]$  and  $[C_{10}mim][Cl]$ ) in  $D_2O$  solutions of various concentrations was studied applying  $^1H$ ,  $^{13}C$  NMR spectroscopy. The time dependencies of integral intensities in NMR spectra indicate that the H/D exchange in  $[C_{10}mim][Br]$  at very high dilution ( $10^{-4}$  mole fraction of RTIL) runs only slightly faster than in  $[C_{10}mim][Cl]$ . The kinetics of this process drastically changes above critical aggregation concentration (CAC). The time required to reach the apparent reaction saturation regime in the solutions of 0.01 mole fraction of RTIL was less 10 h for  $[C_{10}mim][Br]$ , whereas no such features were seen for  $[C_{10}mim][Cl]$  even tens of days after the sample was prepared. The H/D exchange was not observed in the liquid crystalline gel mesophase. Crucial influence of  $Br^-$  and  $Cl^-$  anions on the H/D exchange rates above CAC could be related to the short-range ordering and molecular microdynamics.

**General.** Ionic liquids (ILs)/room temperature ionic liquids (RTILs) can be considered as one of the most successful breakthroughs creating smart materials and multifunctional compositions possessing many appealing features important for the applications in high technologies, including various artificial sensors of new generation, electrochemistry, fuel cells and batteries, (bio-) catalysis, etc. On the other hand, the physical understanding of processes in ionic liquids on a molecular level how the certain peculiar properties may arise from the long-range interionic interactions coupled with their structural features and dynamics is still one of the main challenges for fundamental research. Hydrogen bonding between the anions and cations in certain ILs can play crucial role.

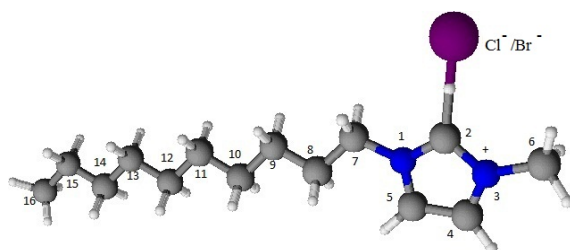


Fig. 1. Molecular structure and carbon numbering of  $[C_{10}mim][X]$ ,  $X = Cl, Br$ .

The purpose of present work was to study the anion effects on the H/D exchange in some of imidazolium-based RTILs, namely – the 1-decyl-3-methyl-imidazolium bromide- and chloride ( $[C_{10}mim][Br]$  and  $[C_{10}mim][Cl]$ ) (Fig. 1) in  $D_2O$  solution applying  $^1H$ ,  $^{13}C$  NMR spectroscopy.

There were 6 samples prepared with  $[C_{10}mim][Cl/Br]$  and heavy water ( $D_2O$ ):  $10^{-4}$ ,  $10^{-2}$ , 0.4 mol. fr. NMR experiments were carried out on BRUKER AVANCEIII HD 400 and BRUKER AVANCEIII 500 NMR spectrometers operating at 400/500 and 100/125 MHz for  $^1H$  and  $^{13}C$ , respectively. The temperature of 298 K was controlled with an accuracy of  $\pm 0.5$  K. The signal of DSS in  $D_2O$  solution and DMSO in capillary insert was used as the reference. The  $D_2O$  and DMSO in the same capillary insert were used for locking. Since in mixtures with water RTILs are tend to form different phases a critical aggregation concentration (CAC) was determined (Fig. 2).

There were nearly no difference in H/D exchange rates in samples of  $10^{-4}$  mol. fr. of both RTILs in  $D_2O$ , reaction was fully finished after 2 days (Figs. 2,3). No difference in exchange rates were observed because samples at this concentration are very similar to classical electrolytes, anions are surrounded by few solvation shells.

In samples of  $10^{-2}$  mol. fr. which is a midpoint between the onsets of aggregation and the gel mesophase formation H/D exchange reaction rates differs dramatically.

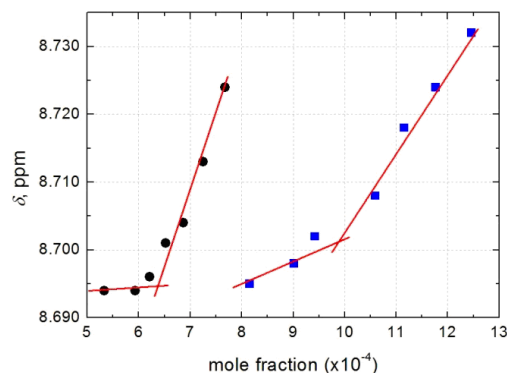


Fig. 2. Determination of critical aggregation concentration (CAC) of  $[C_{10}mim][X]$ ,  $X = Br$  (black circles),  $Cl$  (blue squares) using dependencies of chemical shift of  $C(2)-H$  on concentration in  $H_2O$ .

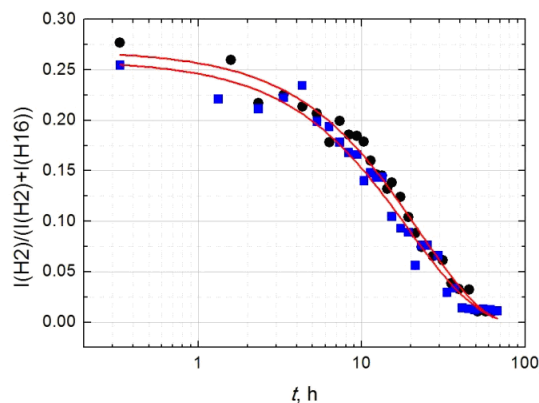


Fig. 3. Kinetics of the H/D exchange reaction in  $[C_{10}mim][X]$ ,  $X=Br$  (black circles) and  $X=Cl$  (blue squares) in  $D_2O$  solutions at high dilution ( $10^{-4}$  mole fraction of RTIL) monitored using the relative integral intensity of  $^1H$  NMR signal of C(2)-H proton respect to the signal of the terminal  $-CH_3$  group.

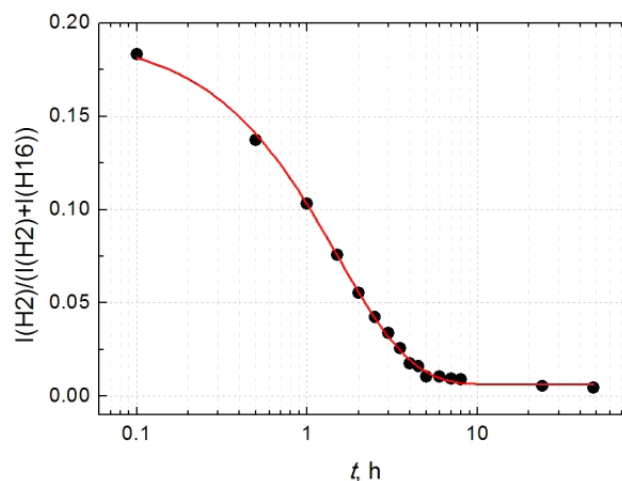
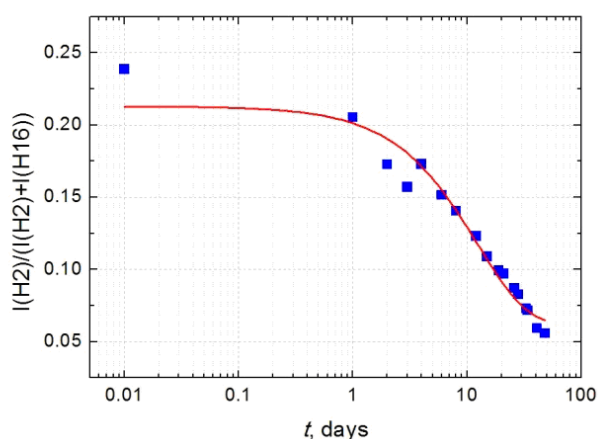


Fig. 4. Kinetics of the H/D exchange reaction in  $[C_{10}mim][X]$ ,  $X = Br$  (black circles) and  $Cl$  (blue squares) in  $D_2O$  solutions at  $10^{-2}$  mole fraction of RTIL monitored using the relative integral intensity of  $^1H$  NMR signal of C(2)-H proton respect to the signal of the terminal  $-CH_3$  group.

The H/D reaction for  $[C_{10}mim][Br]$  took  $8 \div 10$  hours, when in sample from  $[C_{10}mim][Cl]$  even after 48 days of waiting time H/D reaction was not fully finished (Fig. 4). This shows that different micellization processes may damp or increase H/D exchange rates. There were no H/D exchange reaction observed in gel phase samples of 0.4 mol. fr. with both RTILs and  $D_2O$ .

From  $^{13}C$  spectra isotopic effects were assigned when  $C-H \dots Cl^-/Br^-$  protons is changed with deuteriums, a difference of  $^{13}C$  chemical shift vary from 0.25 ppm to 0.02 ppm respectively to the distance to exchanged proton.

The anions and aggregation effects play crucial role in RTIL aqueous solutions. The anions interact with cations via H bonds and bind the water molecules in their solvation shells. The overlap and the competition of these processes may cause rather complex dependency of the H/D exchange reaction rate on the sample composition and on other experimental conditions (temperature, degree of purification, etc).

The H/D exchange process, depending on the anions, can be very significantly damped or stimulated above critical aggregation (micellization) concentration. This reaction does not run in the liquid crystalline gel phase.