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Vibrational sum–frequency generation spectroscopy of ionic liquid 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate at the air–water interface

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ABSTRACT

The structure and orientation of room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [$PF_3(C_2F_5)_3$], commonly known as [bmim][fap], have been investigated at the air–[bmim][fap] and air–water interfaces, employing vibrational sum–frequency generation (VSFG) spectroscopy. The VSFG spectra in the CH stretch region suggest presence of the [bmim] cation at the interfaces. Studies reveal that the butyl chain protrudes out into air, and the imidazolium ring lies almost planar to the interface. The CH stretch intensities get enhanced at the air–water interface, mainly because of polar orientation of imidazolium cation induced by interfacial water molecules. The OH stretch intensities are also enhanced at the air–water interface due to polar orientation of interfacial water molecules induced by [bmim][fap]. The Brewster angle microscopy suggests self aggregation of [bmim][fap] in the presence of water, and the aggregation becomes extensive showing dense surface domains with time. However, the surface pressure is almost unaffected due to aggregation.

1. Introduction

Room temperature ionic liquids (RTILs), which are essentially salts in the liquid phase at room temperature, have several unique properties, such as low volatility, exceptional miscibility, nonflammability, and distinct conductivity, which provide a wide range of applications, for example as green solvents, electrochemical applications and gas-separation technology [1,2]. Therefore, RTILs have offered various research opportunities to investigate their intriguing properties. Since several reactions take place primarily at interfaces, in-depth understanding of the surface properties of RTILs is required. Several techniques have been employed to characterize the surface properties, including aggregation behavior of RTILs in water and other solvents [3,4]. The vibrational sum–frequency generation (VSFG) spectroscopy [5,6], a highly surface selective and sensitive technique, is the most suitable technique to explore the molecular level properties of RTILs at various interfaces. Several research groups have studied structures and orientations of many RTILs at various interfaces using VSFG spectroscopy [7–19]. This technique has been employed to model various interfaces of several alkylimidazolium-based ionic liquids. In general, the VSFG spectra show the CH stretching vibrational modes at higher frequencies than the IR spectra of the bulk liquids for the corresponding peak positions [12]. The shift is consistent with an interfacial structure of RTIL, wherein the alkyl chain orients into the gas/air phase away from the liquid phase. These observations have revealed the structures of the cation and anion of RTILs at various interfaces. The imidazolium ring of the cation lies flat at the interface with the alkyl side chains orienting away from the liquid phase into the gas/air phase [9,10,20]. The cation orientation is demonstrated to be independent of the type of anion [8]. Even at the air–water interface, the imidazolium ring remains nearly parallel to the surface plane without any noticeable change in the orientation in comparison to the gas/air–RTIL interface [18]. And even the cation butyl chain at the air–water interface, remains oriented into the air phase with a slight difference in the orientation angle of CH_3 with respect to the gas/air–RTIL interface. At the SiO_2–RTIL interface, it is reported that the length of the alkyl chain and the surface charge on SiO_2 mainly determine the orientation of the cation at the surface, irrespective of anion composition [21]. It was also shown that the gauche defect depends on the nature of cation and the length of the alkyl chain. At the air–RTIL interface as well, the gauche defects decrease with an increase in the length of the alkyl chain, because of an enhanced interaction between the alkyl chains [12]. At a quartz–RTIL interface as well, the orientation of the cation ring is

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suggested to be almost in the plane of the surface, but found to depend on the size of the anion [22]. The cation ring of a RTIL with a larger sized anion is reported to have a smaller orientation angle with respect to the normal to the surface. Moreover, the orientation of the ring in some of the RTILs is shown to be strongly dependent on the presence of even a trace amount of water. Even at the gas–RTIL interface, the orientation of the ring is found to depend on the hydrophobicity of a RTIL, and its water content [23]. However recently, the water–[bmim][N(SO_2CF_3)$_2$] interface was investigated by VSFG, and no signal was found in the CH stretching frequency region of the [bmim] cation at the interface [13]. Therefore, it was concluded that the [bmim] cation orients weakly or randomly at the interface. At the graphene–RTIL interface as well, the cation, [bmim]$^+$ is shown to be weakly oriented with the alkyl side chain parallel to the graphene plane and the aromatic ring somewhat tilted from the surface plane [24]. Thus, the absence of the VSFG signal for the cation may be due to the effect of anion or the nature of the interface. Moreover, they found that the VSFG spectra of the interfacial anion (due to different conformer) depend on the length of the alkyl chain of the cation. In that case, the VSFG spectra of the interfacial cation should also be influenced by the nature of anion. To the best of our knowledge, the orientation and structure of the imidazolium cation is not investigated in a hydrophobic RTIL [bmim][fap]. We have investigated and compared the structures of [bmim][fap] at the air–[bmim][fap] and air–water interfaces, employing VSFG spectroscopy, surface pressure measurement and Brewster angle microscopy (BAM).

2. Experimental section

2.1. Vibrational sum–frequency generation (VSFG)

Vibrational SFG spectroscopy is a second order non-linear process involving two input beams of visible (ω_{vis}) and infrared frequencies (ω_{IR}), which are fixed at 532 nm, and tunable in 2.3–10.0 μm spectral range, respectively. The experimental details are similar as discussed in our earlier work [25]. Briefly, the fundamental output of a Nd:YAG laser (model: PL2241B, Ekspla, Lithuania) is frequency doubled to generate the visible beam at 532 nm. For generating the tunable IR beam, first an optical parametric generator (OPG, PG401, Ekspla) with a lithium triborate (LiB_3O_5) crystal was pumped by the third harmonic (355 nm) beam of the Nd:YAG laser. Finally, its output was mixed with 1064 nm beam of the Nd:YAG laser in a difference frequency generator (DFG) with a silver thiogallate ($AgGaS_2$) crystal to generate the required tunable IR beam. These two IR and visible laser input beams overlap spatially and temporally at the interface with the angles of incidence at 55° and 60°, respectively. The generated SFG signal beam at the interface was subjected to three stages of filtration (spatial, polarization and spectral) before detection with a photomultiplier tube (PMT). We employed three different polarization schemes of *ssp*, *sps* and *ppp* for the SFG experiments, and these denote the polarization states of the three SFG, visible and IR beams in this sequence.

The VSFG spectra have been measured in the CH and OH vibrational stretching regions by scanning in the range of 2750–3200 cm^{-1} and 3000–3750 cm^{-1}, respectively. Each spectrum was scanned with a step of 2 and 4 cm^{-1} for the CH and OH spectral regions, respectively, with an average of 60 or 100 laser pulses for each experimental point. The VSFG spectra of [bmim][fap] were measured at the air–RTIL interface by taking 3 ml of neat RTIL in a small circular glass trough (~47 mm in diameter and 11 ml volume). For the VSFG spectra at the air–water interface, a special procedure was adopted since [bmim][fap] is almost immiscible in water. Its small amount (3×10^{16} to 15×10^{16} molecules) was thoroughly mixed in a known volume (up to 3 ml) of benzene by ultra sonification, and immediately transferred with the help of a micropipette to a larger circular glass trough (~50 mm in diameter and 16 ml volume), containing 10 ml of water. Before measurements, the mixture was allowed for about 30 m till the benzene solvent completely evaporated. In some experiments, [bmim][fap] was directly spread on the water in the trough using a micro syringe. In all these experiments the circular glass trough was mounted on a six-axis mount for spatial overlapping of the laser beams at the interface. Since [bmim][fap] is highly hydrophobic in nature, we could perform all the experiments with neat RTIL without a need for controlling adsorption of moisture during measurement.

2.2. Surface pressure–time (π–t) adsorption kinetics

We recorded the π–t adsorption kinetics at room temperature (~298 K), employing a platinum Wilhelmy plate microbalance which has an accuracy of ±0.02 mN/m, and the time resolution of $\leqslant$1 s. A fixed amount of [bmim][fap] was added to the circular glass trough (used for VSFG measurement) containing a known volume of Millipore water, and thoroughly mixed. Subsequently, measurements on the π–t adsorption kinetics were initiated. In another experiment a known amount of [bmim][fap] was transferred to a flask containing 2 ml of benzene, and thoroughly mixed. Then the content of the flask was transferred to the glass trough for the surface pressure measurement.

2.3. Brewster angle microscopy

A Brewster angle microscope (BAM, model: Nanofilm_ep3bam, Accurion, Germany) was used for microscopic observation of the surface morphology of [bmim][fap] at the air–water interface. It was mounted on the computer-interfaced microbalance to probe the surface morphology at a particular surface pressure or time. The entire equipment was housed in an acrylic box to avoid any contamination from the environment and to minimize the solvent evaporation. The BAM was equipped with a green laser (532 nm, 50 mW) having *p*-polarized light output, which is completely transmitted and not reflected off from the air–water interface at the Brewster angle of ~53.1°. We optimized the Brewster angle by measuring the reflectivity at the air–pure water interface, and the angle of incidence leading to the lowest reflectivity was taken as the Brewster angle. The appearance of a condensed monolayer phase changes the refractive index and thus, reflectivity to a measurable level. The microscope had the lateral resolution of ~2 μm. The images captured by a CCD camera were digitized and processed for obtaining good quality of BAM pictures by enhancing the contrast. Like surface pressure measurements, two different BAM experiments have been performed by either directly transferring a known amount of [bmim][fap] (3×10^{16} to 15×10^{16} molecules) to the water surface in the glass trough, or by first mixing it in benzene solvent prior to transfer of the mixture to the glass trough.

2.4. Materials

The ionic liquids [bmim][fap] and [bmim][BF_4] (Merck, Germany, purity >99%) were commercial products, and were used without any further purification. The water used was having surface tension of 71.9 mN m^{-1} and resistivity of 18.2 MΩ cm at 298 K, and was prepared using a Millipore apparatus (Millipore, France). We ensured the absence of any hydrocarbon impurity in water by measuring its VSFG spectra.