Intrinsic Mobility of Gaseous Cationic and Anionic Aggregates of Ionic Liquids

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Dedicated to the late J. B. Fenn

Travelling-wave ion mobility mass spectrometry was used to measure the intrinsic mobility of a series of gaseous supra-cation and supra-anion aggregates of several ionic liquids. Close mobilities were observed in a T-wave cell filled with helium at ca. 0.8 mbar for $[(DAI)_{n+1}(X)_n]^+$ (DAI is the 1,3-dialkylimidazolium cation and X is the anion) as compared to the respective anions $[(DAI)_n(X)_{n+1}]^-$ for $n=0$ to 9. The anomalous behavior reported before in the condensed phase seems therefore to be related to the unique structural organization of pure ionic liquids that provides both polar and non-polar regions with directionality in which the anionic species are more retained than the cationic species in the salt network.

1. Introduction

Ionic liquids (ILs), in particular those based on 1,3-dialkylimidazolium cations, are fluids with unique properties such as non-flammability, virtually no vapor pressure, that function as almost universal solvents with high chemical, thermal and electrochemical stability (see Figure 1 for examples).[1,2]
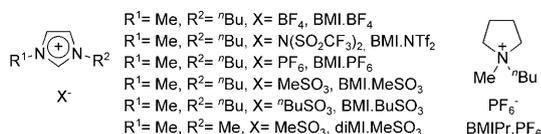

Figure 1. Structure of the IL used in this study.

The properties of ILs are likely related to their unique nanostructure in both the condensed and gas phase.[3] Indeed, ILs display a pronounced and unique self-organization at the molecular level via H-bonded aggregates in the solid,[4] liquid,[5] solution[6–8] and in the diluted gas phase[9] and are consequently highly structured fluids.[10,11]

Imidazolium ILs are therefore supra-ionic fluids and hence are best described as possessing nanostructures of the type $[(DAI)_{n+z}(X)_n)]^{z+}$ and $[(DAI)_n(X)_{n+z})]^{z-}$, where DAI$^+$ is a 1,3-dialkylimidazolium cation and X$^-$ the counteranion.[11] The overall physico-chemical properties of IL are therefore the result of the average properties of these aggregates rather than those of the individual cations and anions. Hence the behavior of the ILs as electrolytes is determined by the transport properties and proportions of the full range of IL aggregates. Consequently, the dynamics and transport properties of the ILs[12–19] is the net effect of combining both the electrostatic and van der Waals forces between all ionic aggregates in the fluid.[17,20] For example, the strong tendency of ILs for clustering[7,21] has

been shown to decrease the number of the charge carriers and to reduce conductivity.[13] Apparently, the geometric shape, size and the delocalization of the ionic charge in the anion are the major factors that determine the magnitude of the transport coefficients.[22,23]

Under equivalent fields, bulkier cations would be expected to diffuse slower than the more compact anions. But interestingly, an anomalous inverted difusibility with cations moving much faster than anions has been reported for pure ILs.[19,24] Direct measurements of IL mobility using an electric field and pulsed gradient spin-echo NMR also found mobilities that were more than an order of magnitude greater than the values estimated from the diffusion coefficients measured under the equilibrium state with no electric field.[25] The ionic

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mobilities of IL measured with or without the field result from random walk and must reflect, as discussed before, the nature and aggregation levels of all supra-ionic species present in the fluid, and the average of their properties. Since the supra-ionic species are therefore not homogeneously structured, it is difficult for NMR or electrochemical approaches to access the structures of the mobile species being measured in the mobility experiments with pure IL, or to estimate whether different mobilities results from the intrinsic properties of these aggregates and/or are mainly dictated by structural effects.

Using travelling wave ion mobility mass spectrometry (TWIM-MS), we report herein the first measurements of the gas phase intrinsic mobilities of individually selected cations and anions and of supra-ionic aggregates up to $n = 9$ of various IL (Figure 1).[5, 26]

2. Results and Discussion

Figures 2 and 3 (bottom) show, as examples, the electrospray ionization mass spectrometry (ESI-MS) (+)-MS or ESI(−)-MS of a methanolic solution of BMI·BF$_4$ (BMI = 1-n-butyl-3-methyl-imidazolium cation).

As previously reported,[7] ESI($\pm$) is able to transfer, directly from the solution to the gas phase, a series of gaseous, intact
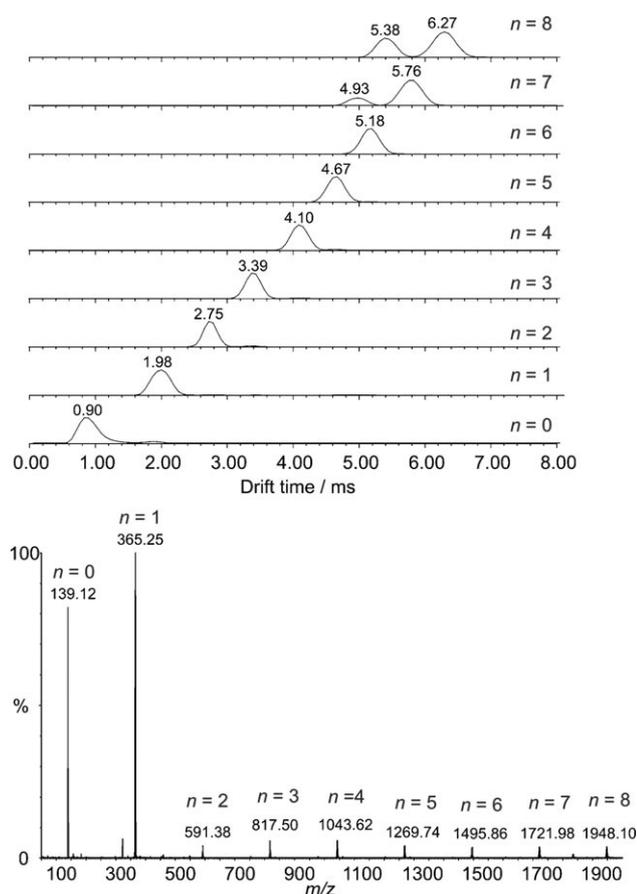
Figure 2. T-wave drift times (top) for BMI + and the supra-cationic aggregates [(BMI)$_{n+1}$(BF$_4$)$_n$]$^+$ transferred directly to the gas phase via ESI(+)-MS (bottom) from a methanolic solution of BMI·BF$_4$
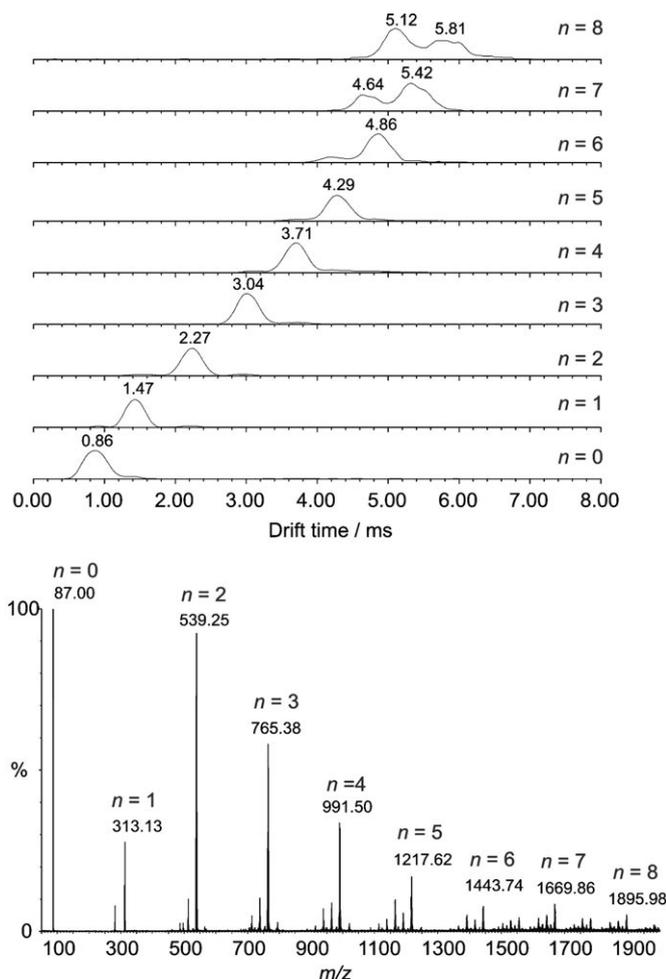
Figure 3. T-wave drift times (top) for BF$_4^-$ and IL supra-anionic aggregates [(BMI)$_n$(BF$_4$)$_{n+1}$]$^-$ transferred directly to the gas phase and selected via ESI(−)-MS (bottom) from a methanolic solution of BMI·BF$_4$.

and singly charged [(BMI)$_{n+1}$(BF$_4$)$_n$]$^+$ and [(BMI)$_n$(BF$_4$)$_{n+1}$]$^-$ aggregates. Fortunately, these loosely H-bonded polymeric supra-ionic networks are conserved to a great extent (up to $n = 9$ for the detectable species) during the gentle ESI ion evaporation process.[27–29] These gaseous species were therefore individually selected and investigated via continuous measurements of their intrinsic gas phase mobilities (drift times, see the Supporting Information) though a T-wave cell filled with helium at a pressure of ca. 0.8 mbar.

Figure 2 (top) shows the drift times for the parent BMI$^+$ and each of the oligomeric supra-cationic aggregates [(BMI)$_{n+1}$(BF$_4$)$_n$]$^+$ as measured rapidly (8 ms) and continually (virtually at the same experimental conditions) from each of such ions. Note the near linear increase of the drift times as a function of the aggregation (n). The extra peaks with higher velocity (lower drift times) for both $n = 7$ and $n = 8$ correspond to the doubly charged species [(BMI)$_{2n+2}$(BF$_4$)$_{2n}$]$^{2+}$ sampled along with the singly charged species [(BMI)$_{n+1}$(BF$_4$)$_n$]$^+$ since they have the same m/z value. As previously reported,[7] ESI($\pm$)-MS is also able to sample large (BMI·BF$_4$)$_n$ aggregates that are able to accommodate two (or even three) additional anions or cat-

ions to form doubly and triply negatively or positively charged supra-ions.

Figure 3 (top) shows the drift times for the anions, that is, BF_4^- and each of the oligomeric anionic aggregates $[(BMI)_n(BF_4)_{n+1}]^-$. These drift times were measured by switching the ESI and MS voltages from positive to negative, and the conditions for the ion mobility measurements were kept virtually the same as those used for the cationic aggregates.[30] The drift times increase again near linearly as a function of the aggregation (n) and, most importantly, both the cationic and anionic aggregates (Figures 2 and 3) with close masses are found to display very close drift times (for instance, for $n = 7$: 1722 Da versus 1670 Da). Again, the extra peaks with higher velocity (lower drift times) for both $n = 7$ and $n = 8$ correspond to the doubly charged $[(BMI)_{2n}(BF_4)_{2n+2}]^{2-}$ species.

Figure 4 summarises all drift times measured for the cationic and anionic aggregates of the various ILs investigated (Figure 1) as a function of their masses (m/z values). Note the
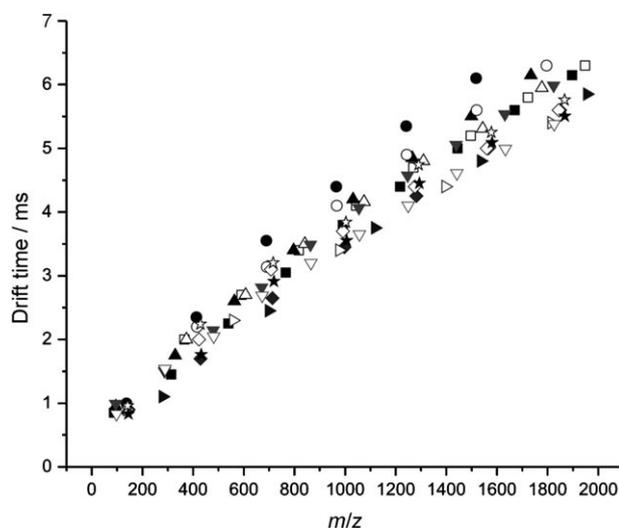
Figure 4. T-wave drift times as a function of the m/z values for cationic (empty symbols) and anionic (solid symbols) aggregates sampled by ESI(±)-MS from methanolic solutions of seven different ILs: BMI·BF₄ (■, □), BMI·MeSO₃ (△, ▲), BMI·BuSO₃ (○, ●), BMI·PF₆ (◇, ◆), BMI·NTf₂ (▷, ▶), diMI·MeSO₃ (▽, ▼) and BMPr·PF₆ (☆, ★).

very close mobilities of the cationic aggregates (empty symbols) compared to the corresponding anionic aggregates (solid symbols). These intrinsic (solvent- and counter-ion-free) gasphase mobilities for each isolated species measured at virtually the same experimental conditions including not only the individual ions, but also a series of their $[(DAI)_{n+1}(X)_n)]^+$ and $[(DAI)_n(X)_{n+1})]^-$ aggregates (up to $n = 9$) indicates therefore that the previous measurements that pointed to a much greater mobility of cations than anions is probably a pure IL-structure-related phenomenon.[20]

Close intrinsic mobilities for the IL aggregates are also indicated by their cross-sections as calculated (Table 1) using the TM model and the MobCal software[31–33] from structures fully optimised at the B3LYP 6-311G(d,p) level using Gaussian 03.

Table 1. Calculated cross-sections in Helium (ΩHe) and experimental drift times for the IL species.

Entry	Species	m/z	ΩHe [Å²]	Drift Times [ms]
1	BMPr⁺	142	78.4	0.96
2	BMI⁺	139	76.7	0.90
3	diMI⁺	97	55.2	0.83
4	NTf₂⁻	280	80.4	1.09
5	BuSO₃⁻	137	68.1	1.03
6	MeSO₃⁻	95	47.8	0.93
7	PF₆⁻	145	50.1	0.90 (0.83)[a]
8	BF₄⁻	87	42.5	0.86
9	[(BMI)₂PF₆]⁺	423	157.1	2.05
10	[(BMI)₂BuSO₃]⁺	415	167.3	2.24
11	[BMI(PF₆)₂]⁻	429	130.7	1.70
12	[BMI(BuSO₃)₂]⁻	413	163.1	2.35

[a] Associated with BMI and BMIPr (in parentheses).

Note that for within the individual cations (entries 1–3) and anions (entries 4–8) as well as their aggregates (entries 9–12) there is a direct correlation of the ΩHe with drift times; that is, the higher ΩHe the higher the drift times. Cations and anions with close ΩHe also display close drift times, as for instance, BMPr⁺ (78.4 Å², 0.90 ms) versus NTf₂⁻ (80.4 Å², 1.09 ms) and [(BMI)₂BuSO₃]⁺ (167.3 Å², 2.24 ms) versus [BMI(BuSO₃)]⁻ (163.1 Å², 2.35 ms). These correlations support the accuracy of the drift time measurements reported herein.

3. Conclusions

The first measurements, under virtually the same experimental conditions, of the intrinsic mobilities of a series of isolated gaseous cations and anions and higher supra-ionic aggregates of several IL are reported. For a T-wave cell filled with helium at ca. 0.8 mbar, close mobilities were observed for DAI⁺ and the $[(DAI)_{n+1}(X)_n]^+$ aggregates as compared to X⁻ and $[(DAI)_n(X)_{n+1}]^-$ aggregates up to $n = 9$. These solvent and counter-ion free intrinsic values oppose to the surprising mobility values measured previously in the condensed phase that have indicated an apparent anomalous greater mobility for the bulkier IL cations.

The calculated ΩHe corroborate the correctness of the gasphase intrinsic drift times reported herein with near linear increase of drift times as a function of ΩHe. When cations are compared to anions, the inversion effect that makes bulkier cations move faster than less crowded anions in pure fluids could not be accounted from their intrinsic properties. The anomalous behavior reported before seems therefore to be related to a structural phenomenon with supramolecular and different polar and non-polar IL domains interactions playing probably the major role.[20]

Experimental Section

The ILs have been prepared and purified using known procedures.[26] The ESI(±)-MS and T-Wave IMMS experiments were performed using a Waters SYNAPT high-definition mass spectrometer (HDMS; Waters Corporation, Manchester, UK) equipped with an ESI

source. More details about this hybrid mass spectrometer and its operation parameters are presented elsewhere.[34,35] In brief, the instrument has a hybrid quadrupole ion mobility orthogonal acceleration time-of-flight (oa-TOF) geometry. Ions are transported to the mobility separation section through the quadrupole analyser, which was operated in the resolving mode. The mobility section comprises three consecutive, gas-filled, travelling wave (T-wave) RF ion guides. Ions are accumulated in the T-wave trap and are periodically released into the T-wave mobility cell, where they separate according to their mobility through the action of a continuous train of DC pulses. The ions exiting the T-wave mobility cell are then transferred to the oa-TOF analyser for MS analysis. The ion drift times were recorded by synchronisation of the oa-TOF MS acquisition with the release of ions from the T-wave trap to the T-wave mobility cell. The ions were released from the T-wave trap every 13 ms for 100 ms. Mass spectra were acquired in the positive and negative ion modes under virtually the same conditions, except for the polarity. The ion source block and nitrogen desolvation gas temperatures were set to 80 and 90 °C, respectively. The T-wave trap and transfer cells were operated at pressures of ~10–2 mbar of Ar, and the T-wave mobility cell was at ca. 0.8 mbar of He. TWIM-MS was done at 450 ms^{-1}, and the DC pulse height was varied from 3.5–27 V. Figure 2 and 3 (bottom) show, as examples, the ESI(+) and ESI(−) mass spectra of a methanolic solution of $BMI.BF_4$.

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