Research Article

Gas-phase dissociation of ionic liquid aggregates studied by electrospray ionisation mass spectrometry and energy-variable collision induced dissociation

Ana M. Fernandes,[a]* João A. P. Coutinho[b] and Isabel M. Marrucho[b]

Positive singly charged ionic liquid aggregates $[(C_n mim)_{m+1}(BF_4)_m]^+$ (mim = 3-methylimidazolium; n = 2, 4, 8 and 10) and $[(C_4 mim)_{m+1}(A)_m]^+$ (A = Cl^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$) were investigated by electrospray ionisation mass spectrometry and energy-variable collision induced dissociation. The electrospray ionisation mass spectra (ESI-MS) showed the formation of an aggregate with extra stability for m = 4 for all the ionic liquids with the exception of $[C_4 mim][CF_3SO_3]$. ESI-MS-MS and breakdown curves of aggregate ions showed that their dissociation occurred by loss of neutral species $([C_n mim][A])_a$ with a ≥ 1. Variable-energy collision induced dissociation of each aggregate from m = 1 to m = 8 for all the ionic liquids studied enabled the determination of $E_{cm,1/2}$ values, whose variation with m showed that the monomers were always kinetically much more stable than the larger aggregates, independently of the nature of cation and anion. The centre-of-mass energy values correlate well with literature data on ionic volumes and interaction and hydrogen bond energies. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

Ionic liquids are salts consisting of one organic cation and one inorganic or organic anion that remain liquid at or near room temperature. The large size and conformational flexibility of the ions lead to small lattice energies and large entropy changes that favour the liquid state.[1] Negligible vapour pressure, non-flammability, wide solvating capability and high thermal, chemical and electrochemical stability are the key properties that generated an increasing interest in the scientific and industrial uses of ionic liquids, mainly as 'green' alternatives to volatile organic solvents.[2] One of the interesting features of ionic liquids is the dependence of their physicochemical properties, such as surface tension, viscosity, melting point and water miscibility, on the type of anion and/or cation. The understanding of this dependence requires knowledge of the interactions between cation and anion in isolated ion pairs as well as the contribution of intermolecular forces for the structural organisation of the liquid phase. Spectroscopic studies and quantum chemical calculations[3–21] published so far for the imidazolium-based ionic liquids have presented evidence for the formation of multiple hydrogen bonds between the H(2), H(4), H(5), H(6), H(7) and the terminal methyl group on the alkyl chain of the imidazolium cation and the anion acceptors. Gas-phase studies on hydrogen bonding between cations and anions have also been performed by fast atom bombardment and electrospray ionisation mass spectrometry.[22–25] X-Ray, ^{1}H NMR, conductivity and microcalorimetry and the data on the interaction between 1,3-dialkylimidazolium cations and several anions have been used to postulate the formation of polymeric supramolecules of the type $\{[(cation)_3(anion)]^{2+}[(cation)(anion)_3]^{2-}\}_n$ through

hydrogen bonding between the cation and anion.[26] The proposed solid state structures are maintained to a great extent in solution and even in the gas phase, as observed by electrospray ionization mass spectrometry,[23,25,27] which enabled the detection of single and multiple negatively and positively charged supramolecules of imidazolium-based ionic liquids as well as the identification of magic numbers in the intensity distribution of ionic supramolecules.[23,25]

The purpose of this work is to investigate the influence of anion type and alkyl chain length of 1,3-dialkylimidazolium-based ionic liquids on the formation and stability to dissociation of aggregates of the ionic liquids listed on Table 1. The unique properties of ESI as a soft ionisation technique, which enables direct transfer of ionised species from solution to the gas phase, combined with variable collision induced dissociation experiments have provided useful information on cluster formation and stability,[28–41] and will also be used in the present study.

* Correspondence to: Ana M. Fernandes, QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: afernandes@ua.pt

a QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

b CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Table 1. Ionic liquids
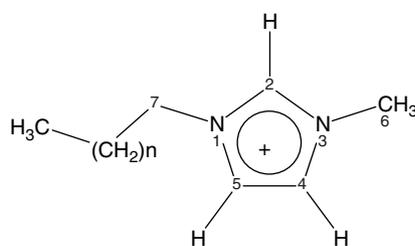
$[C_2mim][BF_4]$	1-ethyl-3-methylimidazolium tetrafluoroborate
$[C_4mim][Cl]$	1-butyl-3-methylimidazolium chloride
$[C_4mim][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate
$[C_4mim][(CF_3SO_2)_2N]$	1-butyl-3-methylimidazolium bis(trifluorosulfonyl)imide
$[C_4mim][CF_3SO_3]$	1-butyl-3-methylimidazolium trifluoromethanesulfonate
$[C_4mim][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate
$[C_8mim][BF_4]$	1-octyl-3-methylimidazolium tetrafluoroborate
$[C_{10}mim][BF_4]$	1-decyl-3-methylimidazolium tetrafluoroborate

Experimental

The ionic liquids listed in Table 1 were purchased from IoLiTec (Freiburg, Germany) or Solchemar (Lisboa, Portugal) and were used without further purification.

Electrospray ionization mass spectra (ESI-MS) were acquired with a Micromass Q-Tof 2 (Micromass, Manchester, UK), operating in the positive-ion mode, equipped with a Z-spray source. Source and desolvation temperatures were 80 and 100 °C, respectively. The ionic liquid solutions in acetonitrile at concentrations $\sim 10^{-4}$ mol dm^{-3} were introduced at a 10 µl· min^{-1} flow rate. The capillary and the cone voltage were 2600 and 25 V, respectively. Nitrogen was used as nebulisation gas and argon as collision gas.

ESI-MS-MS were acquired by selecting the precursor ion with the quadrupole and performing collisions with argon at energies from 3 to 20 eV in the hexapole. The spectra represent an average of approximately 100 scans and the values of $E_{1/2}$ were determined as the collision energy at which the relative abundance of the precursor ion was 50%. Triplicate measurements were performed for each selected precursor ion and standard deviations that varied between 0.3 and 5% were obtained.

Results and Discussion

ESI-MS and magic numbers

The positive-ion mode mass spectra of the ionic liquids studied at concentrations of $\sim 10^{-4}$ M in acetonitrile, shows $[(C_nmim)_{m+1}A_m]^+$ cluster ions for m up to 11 with varying relative abundances. Figure 1 shows a graphical representation of the relative abundance distribution in the positive-ion ESI-MS of $[C_nmim][BF_4]$ ($n = 2, 4, 8$ and 10) in acetonitrile as a function of m. This peak distribution clearly shows, for each cluster ion, a decrease in ion abundance as the alkyl side chain length increases, expressing the expected decreasing tendency for aggregate formation with increasing size of the cation. The usual aggregate ion abundance distribution, which is an exponential decay with increasing m, is not observed here, as also reported in the literature for other imidazolium-based ionic liquids.[23]

These variations in peak intensities are best represented using the scaled intensity proposed by *Zhang* and *Cooks*, where the
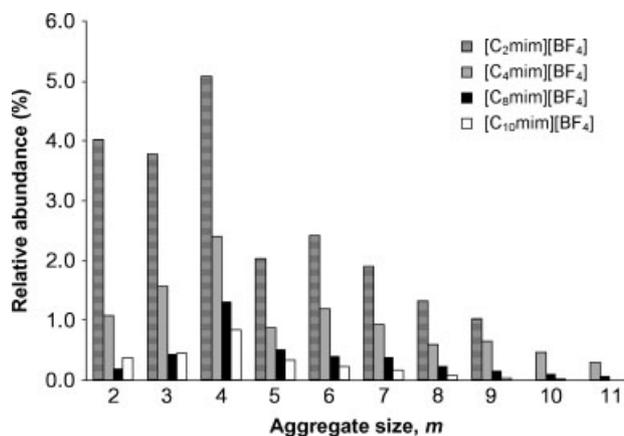

Figure 1. Relative abundance distribution in the positive-ion mode mass spectra of $[C_nmim][BF_4]$ ($n = 2, 4, 8$ and 10) in acetonitrile.

abundances of individual aggregates are compared to those of the neighbours by plotting $I^2_m/(I_{m-1} \times I_{m+1})$ as a function of aggregate size, m, where I is the abundance of the corresponding aggregate ion and the subscript represents the aggregate size.[31] The specific aggregate sizes at which the anomalous abundances occur have been termed 'magic numbers' and are associated with enhanced stability.[42]

The scaled intensity plot is illustrated in Fig. 2 for the ionic liquids with the $[C_4mim]^+$ cation and different anions. Noteworthy in the analysis of Figs 1–2 is the out-of-range abundance of aggregate $[(C_nmim)_5A_4]^+$ for all the ionic liquids studied, with the exception of $[C_4mim][CF_3SO_3]$, indicating a magic number effect, analogous to the previously reported results for other imidazolium-based ionic liquids.[23] It should be pointed out that the monomeric unit of the supramolecular aggregates of ionic liquids in solution identified by other authors[26] is composed of three cations associated with one anion and one cation with three anions, which will be equivalent to the charged species $[(C_nmim)_5A_4]^+$.

The simulation results on cohesive energy of $[C_4mim]$ $[CF_3SO_3]$ clusters,[43] defined as the energy required to split the cluster into its constituent ions, show that the size dependence
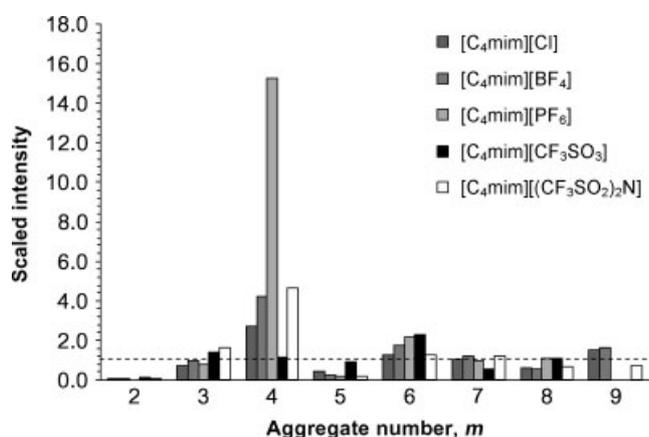
Figure 2. Plot of $I^2_m/(I_{m-1} \times I_{m+1})$ versus aggregate size, n, for [C$_4$mim][A] (A = Cl$^-$, BF$_4$$^-$, PF$_6$$^-$, CF$_3SO_3$$^-$ and (CF$_3$SO$_2$)$_2$N$^-$) ionic liquids.

of the energy is very regular without the apparent stability peaks pointing to a magic number, which agrees with the mass spectral observations reported here for this ionic liquid. The highly symmetric octahedral geometry of hexafluorophosphate anion compared with the other anions might be responsible for the much higher abundance of ion [(C$_4$mim)$_5$(PF$_6$)$_4$]$^+$ (Fig. 2).

Collision induced dissociation of aggregate ions

The fragmentation of the aggregate ions [(C$_n$mim)$_{m+1}$A$_m$]$^+$ of imidazolium-based ionic liquids produced, in all cases, ESI-MS-MS composed of peaks separated by neutral units [C$_n$mim][A]. Since the analysis of the spectra did not allow us to ascertain if the fragmentation took place via sequential losses of neutral units or via one step processes with losses of ([C$_n$mim][A])$_a$ we investigated the dependence on collision energy of the fragment ion abundances for [C$_4$mim][BF$_4$] clusters. The results

thus obtained were represented in the form of breakdown curves as illustrated in Fig. 3 for [(C$_4$mim)$_{m+1}$(BF$_4$)$_m$]$^+$ with $m = 2$ (Fig. 3(a)), $m = 3$ (Fig. 3(b)), $m = 4$ (Fig. 3(c)) and $m = 5$ (Fig. 3(d)), where the percentage of fragment ion abundance relative to the total ion abundance including the precursor, is plotted versus the energy in the centre-of-mass system, E_{cm}, calculated according to Eqn (1) where m_t, m_p and E_{Lab} are, respectively, the target and projectile masses and the laboratory energy.

$$E_{cm} = E_{lab} \left(\frac{m_t}{m_p + m_t} \right) \quad (1)$$

Figure 3(a) clearly indicates that the cation [C$_4$mim]$^+$ is exclusively formed from [(C$_4$mim)$_2$(BF$_4$)]$^+$ since its abundance only increases with the decline of [(C$_4$mim)$_2$(BF$_4$)]$^+$. The breakdown graph of ion [(C$_4$mim)$_4$(BF$_4$)$_3$]$^+$ (Fig. 3(b)) shows co-formation of [(C$_4$mim)$_3$(BF$_4$)$_2$]$^+$ and [(C$_4$mim)$_2$ (BF$_4$)]$^+$ which is an indication that the fragmentation of the precursor ion does not necessarily occur by sequential losses of one neutral unit, but by a direct loss of ([C$_4$mim][BF$_4$])$_2$, this process being predominant because of the greater abundance of the ion thus produced.

Co-formation of ions [(C$_4$mim)$_{m+1}$(BF$_4$)$_m$]$^+$ ($m = 1, 2$ and 3) is also observed, at low collision energies, in the breakdown pattern of the ion [(C$_4$mim)$_5$(BF$_4$)$_4$]$^+$ (Fig. 3(c)), indicating loss of one, two and three neutral units with the formation of ion [(C$_4$mim)$_2$(BF$_4$)]$^+$ prevailing. As the collision energy increases the dissociation pattern resembles that of [(C$_4$mim)$_4$(BF$_4$)$_3$]$^+$ (Fig. 3(b)). The formation, at low collision energies, of low abundant [(C$_4$mim)$_{m+1}$(BF$_4$)$_m$]$^+$ ($m = 1, 2, 3$ and 4) ions may also indicate direct loss of one, two, three and four neutral units from [(C$_4$mim)$_6$(BF$_4$)$_5$]$^+$ (Fig. 3(d)).

Noteworthy in this fragmentation pattern is the higher abundance of the ion [(C$_4$mim)$_5$(BF$_4$)$_4$]$^+$, which corresponds to the monomeric unit of supramolecular aggregates of ionic liquids proposed earlier,[26] indicating an extra stability already evidenced

Table 2. $E_{Lab,1/2}$ values (eV) for [(C$_n$mim)$_{m+1}$A$_m$]$^+$ of imidazolium-based ionic liquids

Ionic liquid	Aggregate size, m							
	1	2	3	4	5	6	7	8
[C$_2$mim][BF$_4$]	8.4	3.9	5.3	7.8	8.1	9.4	10.8	11.7
STDEP[a]	0.14	0.050	0.089	0.079	0.075	0.055	0.094	0.13
[C$_4$mim][BF$_4$]	8.3	4.6	6.1	9.2	9.2	11.8	13.0	13.9
STDEP[a]	0.032	0.053	0.1524	0.096	0.23	0.37	0.20	0.087
[C$_4$mim][Cl]	8.8	5.4	6.7	9.4	8.7	12.0	13.2	–
STDEP[a]	0.076	0.066	0.038	0.17	0.022	0.071	0.16	–
[C$_4$mim][PF$_6$]	8.9	3.9	5.9	9.5	9.4	12.7	14.7	16.0
STDEP[a]	0.11	0.17	0.080	0.21	0.13	0.17	0.097	0.081
[C$_4$mim][(CF$_3$SO$_2$)$_2$N]	8.9	3.5	4.8	7.6	7	9.4	–	–
STDEP[a]	0.034	0.17	0.12	0.14	0.14	0.19	–	–
[C$_4$mim][CF$_3$SO$_3$]	8.5	5.9	6.9	9.0	11.0	12.8	13.0	15.5
STDEP[a]	0.086	0.0061	0.026	0.086	0.098	0.062	0.13	0.15
[C$_8$mim][BF$_4$]	9.3	5.7	8	11.6	12.2	15.6	16.6	19.1
STDEP[a]	0.11	0.098	0.12	0.48	0.27	0.63	0.74	0.80
[C$_{10}$mim][BF$_4$]	10.3	6.5	9.1	12.7	14.4	17.8	19.3	20.4
STDEP[a]	0.17	0.069	0.10	0.45	0.14	0.83	0.57	0.52

[a] Standard deviation calculated using the following formula $STDEP = \sqrt{\frac{1}{N} \sum_{i=1}^{i=N} (x_i - \bar{x})^2}$.
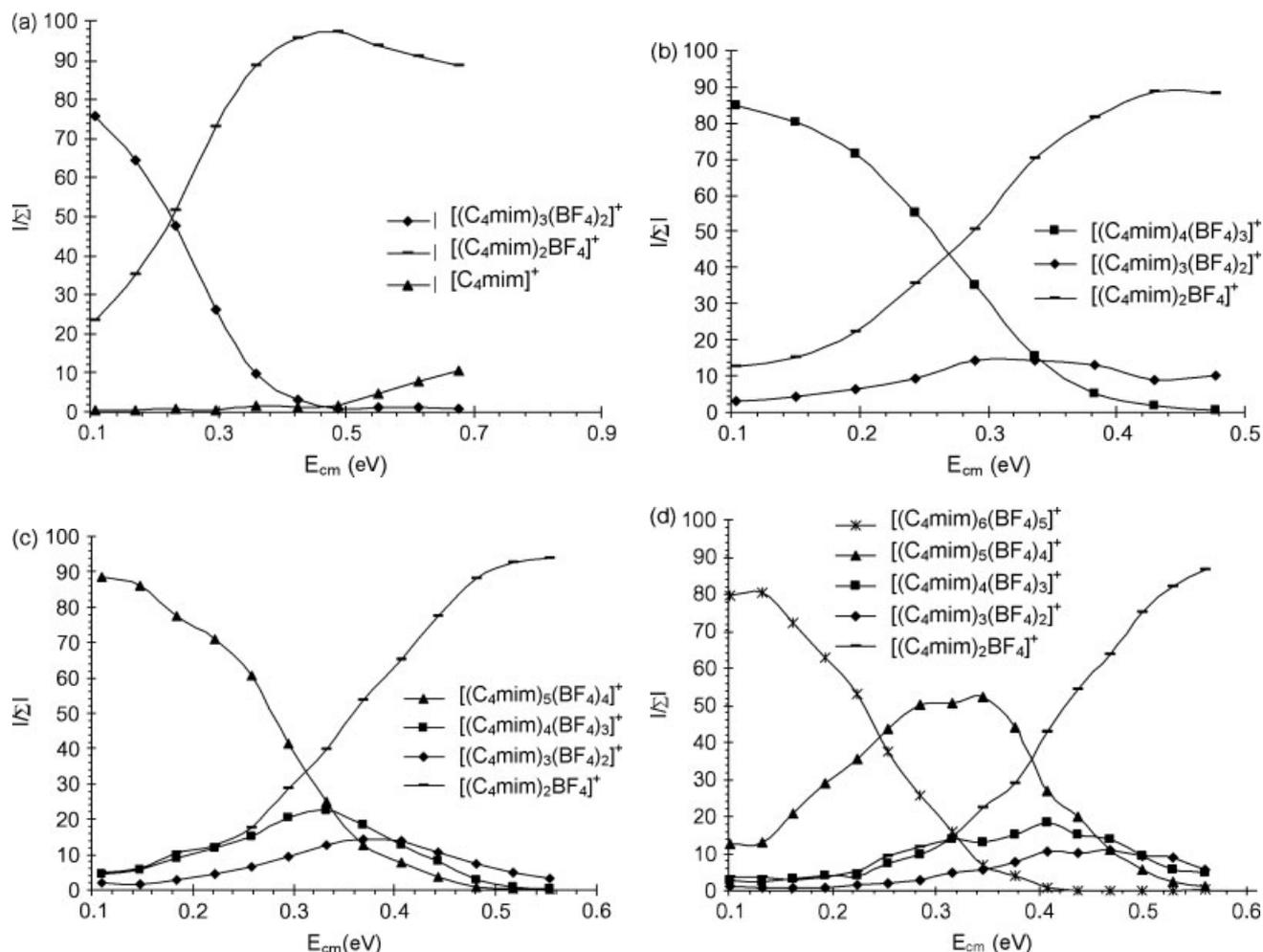
Figure 3. (a) Breakdown curve for ion $[(C_4mim)_3(BF_4)_2]^+$ (b) Breakdown curve for ion $[(C_4mim)_4(BF_4)_3]^+$ (c) Breakdown curve for ion $[(C_4mim)_5(BF_4)_4]^+$ (d) Breakdown curve for ion $[(C_4mim)_6(BF_4)_5]^+$.

by the analysis of the mass spectra of $[C_4mim][BF_4]$. The analysis of the breakdown graphs for the $[(C_4mim)_{m+1}(BF_4)_m]^+$ aggregate ions just presented, point to collision-induced loss of larger neutral $([C_4mim][BF_4])_a$ molecules with $a \geq 1$, and not only a sequential decay of one neutral unit. Changing the anion from tetrafluoroborate to hexafluorophosphate or increasing the length of the alkyl side chain from C_4 to C_{10} does not produce any change in the breakdown patterns.
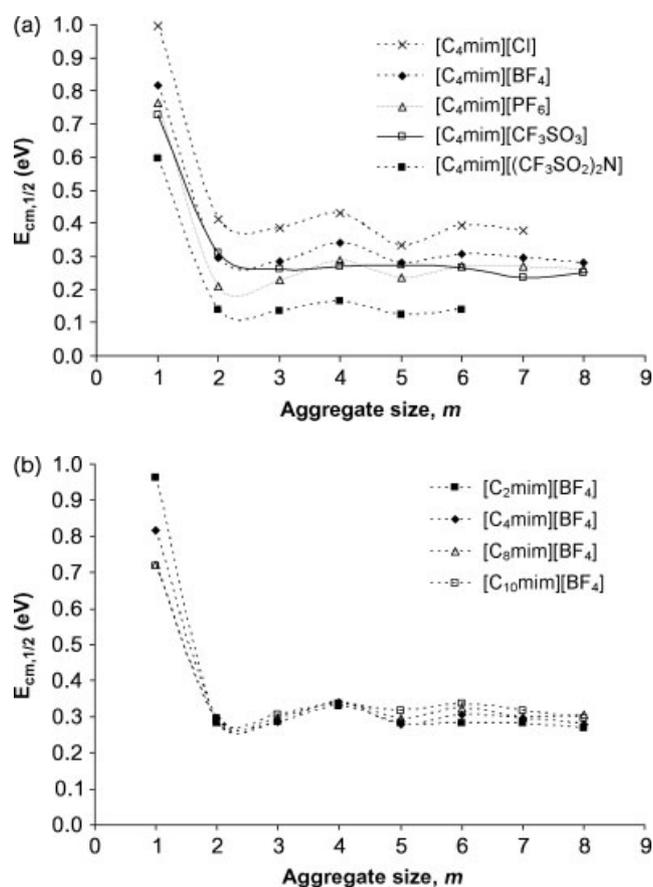
In order to investigate further the influence of N-alkyl side chain length and nature of anion on the kinetic stability of each aggregate ion, a variable-energy collision induced dissociation study was carried out for the $[C_nmim][BF_4]$ ($n = 2,4,8$, and 10) and $[C_4mim][A]$ ($A = Cl^-$, BF_4^-, PF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$) ionic liquid aggregates. ESI-MS-MS of each aggregate ion, for each ionic liquid, were recorded at several collision energies in order to determine $E_{1/2}$, which is here defined as the value of collision energy, in the laboratory frame, at which the relative abundance (defined as percentage of the base peak) of the precursor ion is 50%. Triplicate measurements were performed for each selected precursor ion and standard deviations between 0.3 and 5% were obtained (Table 2).

Figure 4(a) and (b) represents the energy in the centre-of-mass system, $E_{cm,1/2}$ (calculated as described above) as a function of m for the $[C_4mim][A]$ ($A = Cl^-$, BF_4^-, PF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$))

and $[C_nmim][BF_4]$ ($n = 2,4,8$, and 10) ionic liquid aggregates, respectively.

Independently of the cation or anion, the data in Fig. 4(a) and (b) show that the energy necessary to dissociate the monomers ($m = 1$) is much higher than for larger aggregates. From the dimer to the octamer the $E_{cm,1/2}$ values are almost constant, with the exception of the aggregate with $m = 4$, where an increase in energy as compared to its neighbour aggregates is observed. For the ionic liquid $[C_4mim][CF_3SO_3]$ such an increased stability for $m = 4$ is not observed. These results corroborate the observations made previously in the analysis of the mass spectra of theses ionic liquids.
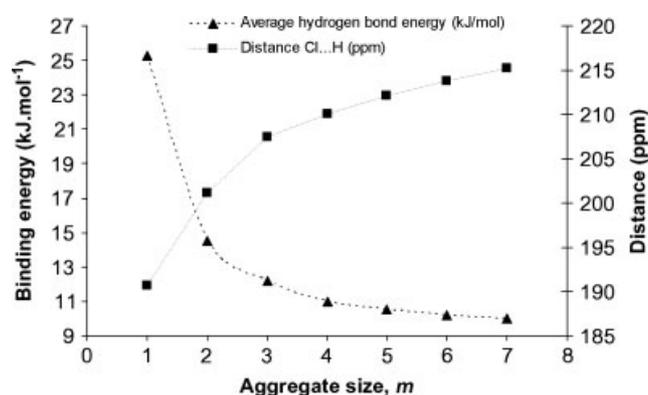
For the discussion of the data presented in Fig. 4(a) and (b), the contributions of Coulomb energy, van der Waals and hydrogen bonding, to the interaction between the cation and anion have to be taken into consideration. According to the data on Fig. 4(a) the order of decreasing energy for the dissociation of the charged monomers $[(C_4mim)_2A]^+$ is: $Cl^- > BF_4^- > PF_6^- > CF_3SO_3^- > (CF_3SO_2)_2N^-$. The opposite trend is followed by the ionic volumes of the anions which, values in $Å^3$ taken directly from Ref. [44], increase in the following order: Cl^- (47) $< BF_4^-$ (73) $< PF_6^-$ (107) $< CF_3SO_3^-$ (129) $< (CF_3SO_2)_2N^-$ (230). The Coulomb interaction energy depends, among other factors, on the intercharge distance which will decrease with anion size

Figure 5. Average hydrogen bond energy per chloride to all protons in kJ mol^{-1} and distance of the chloride to the most acidic proton (data taken from Ref. [21]).

Figure 4. (a) $E_{cm,1/2}$ values for $[(C_4mim)_{m+1}(A)_m]^+$ (A = Cl^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$) ions plotted against aggregate size, m. (b) $E_{cm,1/2}$ values for $[(C_nmim)_{m+1}(BF_4)_m]^+$ ions (n = 2, 4, 8 and 10) plotted against aggregate size, m.

of-mass energy necessary to dissociate the monomer, but its effect on larger aggregates is, in some cases, unnoticeable. For the monomer, $[(C_nmim)_2BF_4]^+$, the increase in chain length will increase the cation–anion distance, decreasing the electrostatic energy as well as the hydrogen bonding strength. Calculations[20] using *ab initio* and density functional theory (DFT) methods on $[C_{1-4}mim][BF_4]$ ion pairs, show a marked increase on the $F\cdots H$ bond length and a decrease in the total interaction energies between the anion and the cation when the *N*-alkyl side chain changes from methyl to butyl. These literature values with smaller cations show a tendency also observed in the mass spectrometric results, since $E_{cm,1/2}$ values decrease in the following order: $[C_2mim]^+ > [C_4mim]^+ > [C_8mim]^+ \approx [C_{10}mim]^+$. The increasing importance of van der Waals forces, as the number of carbon atoms in the *N*-alkyl chain increases, might explain the $E_{cm,1/2}$ value obtained for C_{10}.

Conclusions

The results obtained from the analysis of ESI-MS and variable-energy collision induced dissociation of $[C_nmim][A]$ (mim = 3-methylimidazolium; n = 2, 4, 8 and 10; A = Cl^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$) ionic liquid aggregates were compared with the literature data on calculated interaction energies between cation and anion, ionic volumes and average hydrogen bond energies. The centre-of-mass collision energies $E_{cm,1/2}$ for the dissociation of the charged monomers $[(C_4mim)_2A]^+$ decrease as the ionic volumes[44] of the anions increase and follow the trend of the calculated interaction energies.[45] The increase on the *N*-alkyl side chain length of the monomers $[(C_nmim)_2BF_4]^+$ will cause a decrease in the $E_{cm,12}$ values in agreement with the tendency evidenced by $[C_{1-4}mim][BF_4]$ ion pairs, where a marked increase on the $F\cdots H$ bond length and decrease in the total interaction energies, calculated[20] using *ab initio* and DFT methods, were observed. As the aggregate size increases from m = 1 to 8 for all the ionic liquids studied, the $E_{cm,1/2}$ values show a marked decrease from m = 1 to 2, and remain close to each other from m = 2 to 8, probably because hydrogen bonding will be mainly responsible for the formation of aggregates. This assumption is corroborated by the estimated values[21] of hydrogen bond energy for $[C_1mim][Cl]$ clusters, which show a similar variation with cluster size (Figs 4 and 5).

expressed here by the anionic volume. An increased cation-anion distance will also decrease the contribution of the hydrogen bond to the total interaction energy of the monomer, as evidenced by the published[45] calculated interaction energies of the $[C_4mim]^+$ cation with the anions Cl^-, BF_4^-, and PF_6^- which are −82.0, −77.3 and −71.5 $kcal.mol^{-1}$, respectively. The $E_{cm,1/2}$ values for the monomer (m = 1), which represent its kinetic stability to dissociation are, thus, in good agreement with known calculated values for interaction energies and ionic volumes. The anion effect is also present as m increases from 2 to 8. However the increase in aggregate size is not translated by an increase in the values of $E_{cm,1/2}$, probably because hydrogen bonding will be mainly responsible for the formation of aggregates. Estimation of local hydrogen bonding using the shared-electron number method for $[C_1mim][Cl]$ clusters[21] shows decreasing hydrogen bond energies with an increasing cluster size for both the first hydrogen bond to the most acidic proton of the imidazolium cation and the average hydrogen bond, as well as an increase in the distance of the chloride to the most acidic proton. The hydrogen bond energies and $Cl\cdots H$ distances taken from reference are represented in Fig. 5.

The data in Fig. 5 referring to clusters $([C_1mim][Cl])_m$ also show a marked difference from the monomer to larger cluster sizes, as observed for the $E_{cm,1/2}$ values for the aggregates $[(C_4mim)_{m+1}(A)_m]^+$ and also for $[(C_nmim)_{m+1}(BF_4)_m]^+$ (Fig. 4(b)). The increase in alkyl chain length is clearly visible in the centre-

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