

On the Role of the Dipole and Quadrupole Moments of Aromatic Compounds in the Solvation by Ionic Liquids

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The diverse dipole and quadrupole moments of benzene and its 12 fluorinated derivatives are correlated to their solubility in the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide. Albeit empirical, the correlation was built taken into account molecular insights gained from ab initio calculations of the isolated aromatic solute molecules and molecular dynamics simulations of all 13 aromatic solute plus ionic liquid solvent binary mixtures. This type of molecular-assisted approach unveiled a simple correlation between the dipole and quadrupole moments of the solutes and the ionic liquid solvent. It also revealed the complex nature of the interactions between aromatic compounds and ionic liquids, with the charge density functions of the former acting as a sort of molecular template that promotes the segregation of the ions of the latter and defines the fluid phase behavior (liquid–liquid demixing) of the corresponding binary mixtures. Such an approach can be extended to other systems involving the interactions of different types of solutes with ionic liquid solvents.

1. Introduction

This work aims at understanding how ionic liquids work as solvents in interaction-rich systems. It focuses on the solvation of aromatic compounds of varying polarity in ionic liquids. Experimental information, including solubility, phase diagrams, and structural data, is now available for the entire series of fluorinated benzenes in the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide, [C₂mim][NTf₂]. This aromatic series is composed of 13 molecules ranging from benzene to perfluorobenzene and includes all possible partially fluorinated species. Such a rich data set provides a unique test ground for studying the roles of the dipole and quadrupole moments on the interactions of aromatic molecules with an ionic liquid, and thus improves our fundamental knowledge of these sophisticated solvents. Ionic liquids are not simple fluids: they are composed of asymmetric, flexible ions with delocalized electrostatic charges and a presence of both charged and nonpolar groups in their molecular structures. Their behavior as solvents is a consequence of a balance between Coulomb and van der Waals forces, a fact that can lead to structurally heterogeneous liquids.¹

The solubility of benzene and other arenes in [C₂mim][NTf₂] was first reported by Lachwa et al.² Very recently, Shiflett and Yokozeki³ measured the solubility of benzene and of its 12 fluorinated derivatives in the same ionic liquid. In this comprehensive study, the authors were able to fit the experimental liquid–liquid equilibrium data to the NRTL (nonrandom two liquids) solution model and also to establish a general empirical correlation between the dipole moment of the aromatic solutes

and the immiscibility gaps in the corresponding mixtures with ionic liquids. However, that general trend did not hold for many of the aromatic compounds with null or small dipole moments and the authors admitted that it would be necessary to consider additional intermolecular interactions. They stated that “This poses a unique and interesting challenge for theoretical modelers to explain these measurements.” In this work, we have decided to accept that challenge. We have used ab initio calculations and molecular dynamics simulations to explain from a molecular perspective the rather complex behavior of the binary mixtures of the ionic liquid [C₂mim][NTf₂] with benzene and its 12 fluorinated derivatives, and we believe that the insights obtained in the present work are general and applicable to interpret results of other solutions and mixtures involving ionic liquids. Simulations of mixtures of ionic liquids with benzene and some of its fluorinated derivatives were first reported by Lynden-Bell and co-workers.⁴

In recent studies, we also discussed the liquid–liquid and solid–liquid phase behavior of binary mixtures of different ionic liquids with benzene and two of its fluorinated derivatives, hexafluorobenzene and 1,3,5-trifluorobenzene.⁵ The corresponding phase diagrams have shown liquid–liquid immiscibility windows completely shifted toward aromatic-rich compositions; i.e., the three studied aromatic compounds are quite soluble in the pure ionic liquids, but no measurable amount of the latter can be dissolved in any of the pure aromatic compounds. The phase diagrams also exhibited different kinds of interesting solid–liquid behavior, ranging from the occurrence of eutectic points, the existence of congruent melting points and the corresponding formation of inclusion crystals, or the observation of different ionic liquid crystalline phases (polymorphism). The different types of phase behavior were probed at a molecular level using X-ray diffraction techniques and by molecular dynamics simulations.⁵ The structural data thus obtained

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TABLE 1: Dipole Moment (μ), Molecular Quadrupole Moment (Q_{ii}), Mass Density (ρ), and Solubility (Mole Fraction (x) and Volume Fraction (ϕ)) of Benzene and Its 12 Fluorine-Substituted Derivatives in the 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid^a

compound	code	μ , 10 ³⁰ C·m	Q_{xx} , ^b 10 ⁴⁰ C·m ²	Q_{yy} , ^b 10 ⁴⁰ C·m ²	Q_{zz} , ^b 10 ⁴⁰ C·m ²	ρ , kg·dm ⁻³	solubility	
							x	ϕ
benzene	0	0	14.6	14.6	-29.2 (-28.2)	0.875	0.76	0.52
1,4-difluorobenzene	14	0	-36.6	43.8	-7.3	1.146	0.82	0.64
1,3,5-trifluorobenzene	135	0	-1.2	2.3	-1.1 (3.3)	1.268	0.50	0.29
1,2,4,5-tetrafluorobenzene	1245	0	-45.7	32.1	13.6	1.421	0.74	0.54
hexafluorobenzene	123456	0	-16.8	-16.8	33.6 (31.6)	1.612	0.66	0.46
fluorobenzene	1	5.82 (5.33)	26.8	-5.9	-20.9 (-21.0)	1.022	0.87	0.71
1,3-difluorobenzene	13	5.76 (5.03)	27.8	-17.8	-10.0	1.139	0.75	0.54
1,2,4-trifluorobenzene	124	5.55	-35.1	33.8	1.2	1.280	1.00	1.00
1,2,3,5-tetrafluorobenzene	1235	5.44	-23.3	11.9	11.4	1.403	0.65	0.44
pentafluorobenzene	12345	5.42 (4.79)	10.7	-32.7	22.0	1.511	0.70	0.50
1,2-difluorobenzene	12	9.80 (8.19)	-3.3	17.4	-14.0	1.156	1.00	1.00
1,2,3-trifluorobenzene	123	11.20	13.2	-8.4	-4.7	1.292	1.00	1.00
1,2,3,4-tetrafluorobenzene	1234	9.54	22.9	-31.2	8.3	1.408	1.00	1.00

^a The three groups correspond to molecules with null dipole moment, with dipole moments similar to that of fluorobenzene, and with large dipole moments, respectively. The solubility data at 300 K were taken from ref 3. Available experimental values of μ and Q_{zz} are given between parentheses for comparison purposes (see text). ^b The quantities Q_{ii} correspond to the three non-null and traceless components of the molecular quadrupole moment tensor. The z direction is normal to the aromatic plane, and Q_{zz} is usually referred to as the aromatic quadrupole moment. The x and y directions are given in Figures 2, 5, and 7.

revealed the interactions of ionic liquids with aromatic compounds, and how these are affected by the nature of the aromatic compounds (namely, the reversal of the molecular quadrupole moment when switching from benzene to hexafluorobenzene), the aromatic or nonaromatic character of the cation of the ionic liquid, and the size of the corresponding anion.

2. Computational Details

Ab Initio Calculations. Multipole moments and electrostatic charge distributions were calculated using Gaussian 03⁶ at the MP2/cc-pVTZ(-f)//HF/6-31G(d) level of theory, thus using the same basis set as in the OPLS-AA model for perfluoroalkanes⁷ and for ionic liquids.^{8,9} The cc-pVTZ(-f) basis set¹⁰ was used for single-point energy calculations in geometries optimized at the HF/6-31G(d) level, as is current practice in the development of force field parameters for molecular simulation.^{11,12} For the C and N atoms, the cc-pVTZ(-f) basis set is created by removing the f functions from the definition of the triple-cc-pVTZ basis set of Dunning.¹⁰ The combination of the levels of theory and basis sets used here has been tested on a large collection of molecules (Halgren test) and was demonstrated to yield accurate conformational energetics.¹³ It must be stressed that no constraints were placed in any of the molecules during geometry optimization or point charge calculation in order to reproduce a specific molecular moment. The point is that, although the theoretical results give slightly overestimated dipole and quadrupole moments (see the Results and Discussion section below), they form a consistent set for the 13 aromatic molecules under discussion. Moreover, and given the empirical nature of the correlation that will follow (see Results and Discussion), any differences between the experimental and theoretical electrical moments will be absorbed by the fitting of the empirical parameters.

Molecular Dynamics Simulations. The molecular force field used to represent the ionic liquids is based on the OPLS-AA model¹⁴ but with parameters specifically tailored for the ions in question.^{8,9} Following the spirit of OPLS-AA, intramolecular terms related to covalent bonds and angles are taken from the AMBER force field,¹¹ and efforts are concentrated on carefully describing conformational and intermolecular terms. Benzene and its derivatives were represented also within the OPLS

framework using the parametrization proposed by Jorgensen¹⁴ and the CHelpG charges obtained in this work (see previous section). The full set of parameters is given as Supporting Information. All simulations were performed using molecular dynamics algorithms, implemented in the DL_POLY program.¹⁵ In the case of the benzene and hexafluorobenzene mixtures, we started from low-density initial configurations, composed of 192 ion pairs and 64 solute molecules—an ionic liquid mole fraction of 0.75. These were equilibrated at constant NpT for 500 ps at 300 K using a Nosé–Hoover thermostat and barostat with time constants of 0.5 and 2 ps, respectively. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive–dispersive interactions were explicitly cut off at 16 Å (long-range corrections were applied assuming the system had a uniform density beyond this cutoff radius). The final configurations of these pre-equilibrated systems, namely, the one containing hexafluorobenzene, were used to generate the initial configurations of all other systems containing the partially fluorinated benzene solutes, also with ionic liquid mole fractions of 0.75. Further simulation runs of 100 ps were used to produce re-equilibrated systems at the studied temperatures. Finally, 1000 configurations were stored from production runs of 300 ps for each one of the possible 13 systems. Successive 300 ps runs of each system showed no drift in the corresponding equilibrium properties at this stage. The stored configurations for each system were used to generate the spatial distribution functions (SDFs) presented.

3. Results and Discussion

The molecular dipole moment, μ , and the three principal-axis components of the molecular quadrupole tensor, Q_{xx} , Q_{yy} , and Q_{zz} , of benzene and its 12 fluorinated derivatives were calculated from the corresponding electron density obtained *ab initio* (see methods section below for computation details). The results, presented in Table 1, compare well with other sets of data obtained either from experimental or quantum-mechanical studies.^{16–21} Reference 16 (Hernandez-Trujillo and Vela) is the only set of data found in the literature that contains μ , Q_{xx} , Q_{yy} , and Q_{zz} for benzene and all of its 12 fluorinated derivatives. In order to preserve the self-consistency of the correlation procedure that follows, we decided to use exclusively our own set of

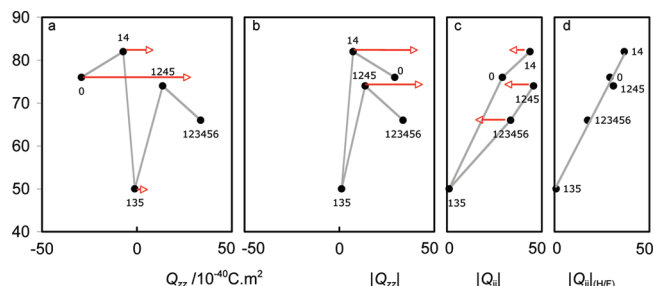


Figure 1. Correlations between the solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ of benzene and its four fluorine-substituted derivatives with null dipole moment (cf. Table 1) and their electric quadrupole moments: (a) aromatic quadrupole moments; (b) moduli of aromatic quadrupole moments; (c) moduli of the largest component of the quadrupole tensor; (d) part c corrected for the difference between anion–hydrogen and cation–fluorine interactions (see text).

multipole moments and the solubility data reported by Shiflett and Yokozeki³ (also presented in Table 1).

We have considered first only those compounds with null dipole moment (the first group of five compounds in Table 1). This allowed us to separate the influence of the molecular dipole and quadrupole moments on the solubility of the compounds. Figure 1 outlines the different steps taken to achieve a correlation between the molecular quadrupole and solubility data.

A plot of the solubility in the ionic liquid of the five aromatic compounds as a function of their aromatic quadrupole moment, Q_{zz} (Figure 1a), shows a zigzag pattern and a first warning concerning the complexity of the task in hand. The situation is improved if one recognizes that the sign of the aromatic quadrupole moment is irrelevant: both benzene and perfluorobenzene, with their equivalent but opposite quadrupole moments, are more soluble than 1,3,5-trifluorobenzene, which has an almost null quadrupole. Benzene and perfluorobenzene are able to permeate the cohesive ionic network in a more effective way, by adopting configurations with the anions and cations of the ionic liquid clearly localized in the polar and equatorial positions of the aromatic ring.⁵ In the case of benzene, cations occupy the polar positions and anions the equatorial regions; the situation is reversed for hexafluorobenzene. This can be seen in Figures 2 and 3 where we have plotted charge–density profiles of the five aromatic compounds under discussion (calculated *ab initio* for the isolated molecules) and spatial probability distribution functions of the ionic liquid ions around them (obtained by MD simulation of the condensed phases), respectively.

The most conspicuous feature revealed by the comparison of Figures 2 and 3 is the complementary nature of the electrostatic charge distribution on the aromatic molecules (Figure 2) and the most probable arrangement of ions around them (Figure 3): the ions of the ionic liquid organize themselves around the aromatic molecules (or the latter permeate the polar network formed by the former) in a way that Coulomb interactions are maximized—blue areas in Figure 2 are matched by red areas in Figure 3 and vice versa. In other words, the charge distribution in the aromatic molecules can be seen as a template that is used by the ions of the ionic liquid to reorganize themselves and allow (in larger or smaller quantities) the dissolution of the aromatic solutes in their midst.

The arrangement of ions around benzene and hexafluorobenzene are complementary but essentially analogous (Figure 3, far-left and far-right images) with ions of opposite sign occupying the polar and equatorial positions around the aromatic ring. In order to correlate solubility with the aromatic quadrupole

moment, one should take the modulus of the latter quantity: $|Q_{zz}|$ instead of Q_{zz} (this corresponds to flipping three points in Figure 1a (indicated by the red arrows), yielding Figure 1b). Unfortunately, 1,4-difluorobenzene (14) and 1,2,4,5-tetrafluorobenzene (1245) do not fit into this simple scenario (Figure 1b): the moduli of their aromatic dipole moments are smaller than those of benzene and hexafluorobenzene, but their solubilities in $[\text{C}_2\text{mim}][\text{NTf}_2]$ are larger. This contradiction can be corrected by looking again at Figures 2 and 3. Around (14) and (1245), the ions of the ionic liquid are not located on the polar and equatorial positions of the aromatic molecule but along another axis of the molecule. In other words, the molecular quadrupole moment that should be considered in these cases is not the aromatic one, $|Q_{zz}|$, but one of the other two components of the quadrupole tensor, $|Q_{xx}|$ or $|Q_{yy}|$, that governs the placement of ions around the aromatic molecule: $|Q_{yy}|$ in the case of (14) and $|Q_{xx}|$ in the case of (1245). The rule behind this choice is clear: it is the largest component of the quadrupole tensor that controls the spatial distribution of ions. When the largest component of the quadrupole moment is taken into account, the points in Figure 1b corresponding to (14) and (1245) shift to the left (red arrows) and Figure 1c is obtained. In the new plot, there are two trends: one corresponding to hydrogenated or predominately hydrogenated compounds, the other to those in which the degree of fluorination is higher. The reason is that, although the fluorinated or hydrogenated benzenes display almost symmetrical electrostatic charge distributions (cf. Figure 2), their molecular sizes and interactions with the ions of the ionic liquid are not completely equivalent. The solubility of benzene is higher than that of hexafluorobenzene in spite of the almost identical absolute values of quadrupole moment, and the same is true when comparing (14) with (1245). These differences are recognizable in Figure 3, where the oxygen of the anions interacts with the hydrogen atoms of the aromatic compounds in a much more localized way (red areas) relative to the fuzzier blue patches corresponding to the interactions between the fluorine atoms of the aromatic compounds and the cations. In fact, in previous studies where 1:1 inclusion crystals of benzene and $[\text{C}_2\text{mim}][\text{NTf}_2]$ could be isolated, X-ray diffraction results showed that the interactions between the oxygen atoms of the anion and the hydrogen atoms of benzene are similar to a hydrogen bond. The same is not true for the cation–fluorine interactions in mixtures of $[\text{C}_2\text{mim}][\text{NTf}_2]$ with hexafluorobenzene, where no inclusion compound was ever found. To take into account the difference between the hydrogen and fluorine interactions in the present study, one single empirical fitting parameter is required: we found that, if we fit such an (H/F) parameter in a way that each fluorine substitution decreases the effectiveness of the quadrupole moment of the molecule by 8% ($|Q_{ij}|_{(H/F)} = |Q_{ij}|(1 - 0.08N_F)$, where N_F is the number of fluorine atoms substituted in the benzene molecule), the points in Figure 1c shift in such a way (red arrows) that they will all lie on one straight line (Figure 1d).

The second phase of the correlation process is to incorporate the five other benzene derivatives that, due to the sixfold symmetry of the aromatic ring, have dipole moments similar to that of fluorobenzene. With this group of molecules, we can check how interactions of an almost constant dipole moment affect (or are affected by) the different molecular quadrupole moments of each molecule. Figure 4 is similar to Figure 1 in the sense that it also shows the different steps that were taken to incorporate the new points into a general correlation scheme. Figure 4a shows the solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ of the second group of five benzene derivatives as a function of their aromatic

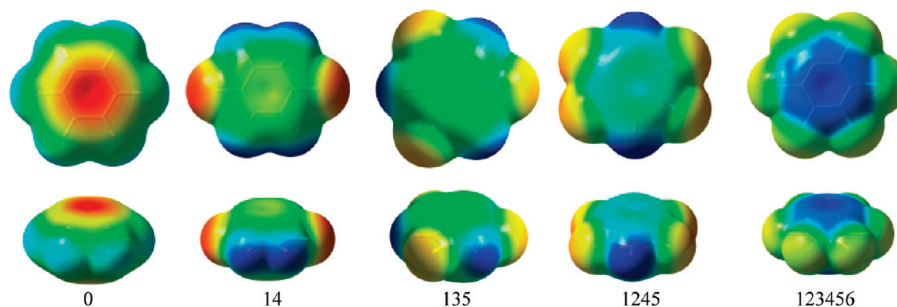


Figure 2. Electrostatic potential mapped onto an electron density isosurface around the five aromatic molecules with null dipole moment. Positively or negatively charged regions are indicated by color gradients changing from dark blue to red, respectively. From left to right: benzene, 1,4-difluorobenzene, 1,3,5-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, and hexafluorobenzene. Top row: frontal views of the aromatic molecules with the x -, y -, and z -axes oriented horizontal, vertical, and normal to the sheet directions, respectively. Bottom row: side views of the molecules with the z -axis oriented in an almost vertical direction.

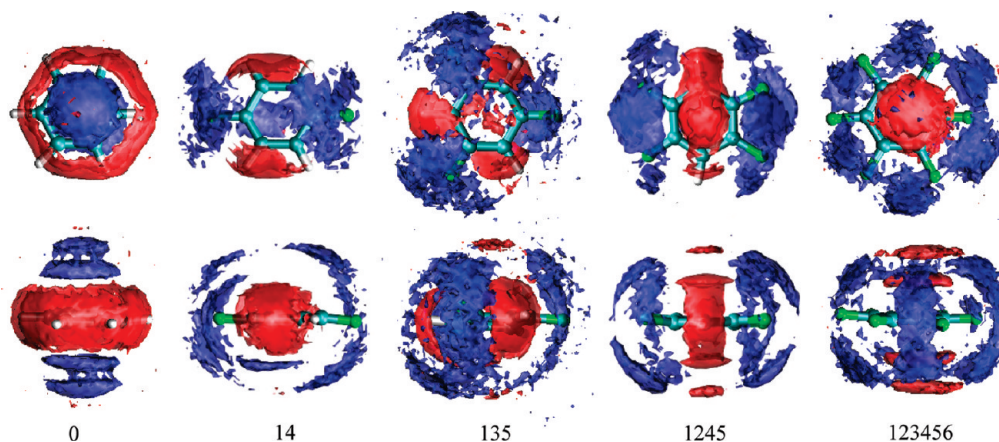


Figure 3. Spatial distribution functions of selected atoms of $[\text{C}_2\text{mim}][\text{NTf}_2]$ around the five aromatic molecules with null dipole moment, in mixtures containing a mole fraction of 0.75 in ionic liquid. The nature and orientation of the five aromatic molecules are the same as those represented in Figure 2. The images show in red the distribution of the oxygen (O) atoms of the bistrifluoromethanesulfonate anion (sites of negative partial charge) and in blue the C2 carbon of the imidazolium ring (a site of positive partial charge) around a central aromatic molecule. The isosurfaces depicted correspond to relative densities of 1.8 for O and 2.2 for C2, relative to the average densities of those atoms in the mixtures.

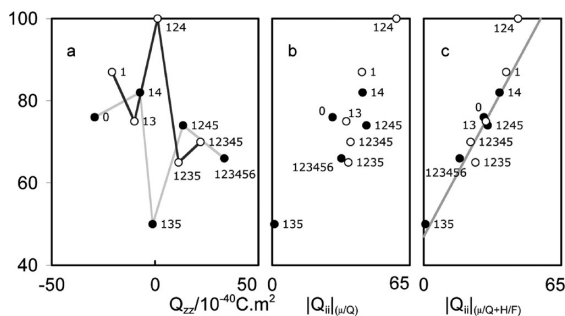


Figure 4. Correlations between the solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ of benzene and nine of its fluorine-substituted derivatives with null or low dipole moment (cf. Table 1) and their electric quadrupole moments: (a) aromatic quadrupole moments; (b) moduli of the adequate component of the quadrupole moment tensor corrected for the countereffect of the dipole moment (see text); (c) part b corrected for the difference between anion–hydrogen and cation–fluorine interactions.

quadrupole moments, superimposed on the same representation of the first group of already studied benzene derivatives. The situation is not very encouraging, since this time a new zigzag dependence appears but in the reverse sense of the one observed for the benzene derivatives with null dipole moment. The relationship between the dipole and quadrupole moments of each molecule and their mutual influence on its solubility in the ionic liquid is far from trivial and must be again analyzed in terms of the corresponding charge distributions of the isolated molecules and the spatial distribution functions of the ions in the liquid mixtures, Figures 5 and 6, respectively.

The two zigzag patterns of Figure 4a show that the presence of a permanent dipole moment in the molecules increases their solubility in the ionic liquid (the open circles are, on average, above the full ones) but that the increase is more pronounced when the corresponding aromatic quadrupole moment is almost null. The effect is extreme for 1,3,5-trifluorobenzene, which has the lowest solubility in the ionic liquid, and for 1,2,4-trifluorobenzene, which is completely soluble in the ionic liquid at room temperature. In other words, when both are present, the effects of the dipole and quadrupole moments of the solute have antagonistic effects: when there is no permanent dipole moment, the solubility is directly proportional to the intensity of the largest component of the quadrupole moment of the molecule, but when a permanent dipole moment is present, the solubility decreases concomitantly (and explains the two opposed zigzag patterns).

Figures 5 and 6 show again the complementary nature of the charge distributions in the aromatic molecules (Figure 5) and the resulting solvation spheres of ions around them (Figure 6). They also show the interplay between the dipole moment of the molecule and the three components of the quadrupole moment tensor (which now is affected by the presence of the permanent dipole moment, especially in the Q component that is aligned with μ). For instance, we can see that in fluorobenzene the effect of the dipole moment is to segregate the solvating ions of the ionic liquid along its x -axis direction, as shown in Figure 6 (SDFs at the far left), but that this organization of the solvent ions is perturbed by the presence of the aromatic

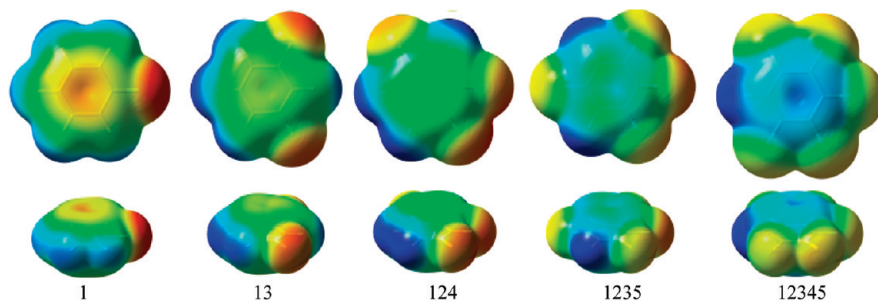


Figure 5. Electrostatic charge distribution around the five aromatic molecules with dipole moments between 5.42×10^{-30} and $5.82 \times 10^{-30} \text{ C}\cdot\text{m}$. From left to right: fluorobenzene, 1,3-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, and pentafluorobenzene. Top row: frontal views of the aromatic molecules with all of the dipole moments pointing to the right. The x -, y -, and z -axes are oriented horizontal, vertical, and normal to the sheet directions, respectively, except for 1,2,4-trifluorobenzene (in the middle) where the x -axis is not aligned with the dipole moment (it deviates around 45° from it). Bottom row: side views of the molecules with the z -axis oriented in an almost vertical direction. Positively or negatively charged areas are indicated by color gradients changing from dark blue to red, respectively.

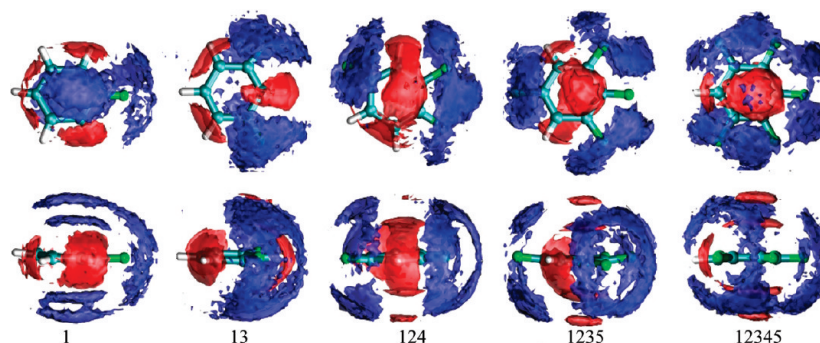


Figure 6. Spatial distribution functions of atoms of $[\text{C}_2\text{mim}][\text{NTf}_2]$ around the aromatic molecules in mixtures with the five aromatic molecules with a dipole moment similar to that of fluorobenzene. The nature and orientation of the five aromatic molecules are the same as those presented in Figure 5. The color coding is the same as that in Figure 3.

quadrupole moment (z -axis direction) that also leads to a segregation of solvating cations to the polar region and of anions to the equatorial region around the solute. The result is a combination of effects illustrated by the above-mentioned SDFs. Similar situations are observed for all other derivatives. A special case is that of 1,2,4-trifluorobenzene, which has an almost null aromatic quadrupole moment (Q_{zz}) and where the other two components of the quadrupole moment are partially aligned with the permanent dipole. In this case, the solvating ions are segregated in a very clear-cut manner (partially aligned with the dipole) explaining the enhanced solubility of this molecule relative to the other four members of this group of fluorinated benzenes.

In order to obtain a sufficiently general empirical correlation that includes these new insights and is capable of predicting the solubility of all of the benzene derivatives studied so far, a second empirical parameter was introduced in order to capture the opposing effects of the dipole and quadrupole moments of the solute molecule. We have found that an effective quadrupole moment, $|Q_{ii}^{\mu/Q}|$, can be obtained empirically if the permanent dipole moment of the molecule is multiplied by a factor of 1.1 nm and the appropriate molecular quadrupole moment of the molecule (not necessarily the aromatic one) is deduced from the result, $|Q_{ii}^{\mu/Q}| = (1.1 \times 10^{-10} \mu - |Q_{ii}|)$. Taking into account the charge and ion distributions presented in Figures 5 and 6, we have used values of $|Q_{zz}|$ in the case of fluorobenzene and pentafluorobenzene and $|Q_{xx}|$ for 1,3-difluorobenzene and 1,2,3,5-tetrafluorobenzene. For 1,2,3-trifluorobenzene, we have used its value of $|Q_{zz}|$, since in this case the other two components of the quadrupole tensor (xx and yy) are almost symmetrical and are both partially aligned with the dipole moment vector (see above).

When the $|Q_{ii}^{\mu/Q}|$ expression is used on the points of Figure 4a, they shift to yield Figure 4b. Again, two series of points appear corresponding to compounds with a different degree of fluorination. If the same (H/F) correction already used in the compounds with null dipole moment is applied to the new, more complete set, the points are shifted again to yield Figure 4c, where all 10 compounds considered so far lie close to a straight line:

$$100x(\text{C}_6\text{H}_i\text{F}_{6-i}) = (|Q_{ii}^{\mu/Q}|_{\mu/Q+H/D})/10^{-40} \text{ C}\cdot\text{m}^2 + 46 \quad (1)$$

Finally, if the three remaining benzene derivatives are taken into account (Figures 7 and 8) and their effective quadrupole moments, $|Q_{ii}^{\mu/Q}|_{\mu/Q+H/D}$, are calculated considering the (μ/Q) and (H/F) corrections, eq 1 will yield solubility values above 100%. This means that the correlation is correctly predicting the complete miscibility of these three compounds with the ionic liquid. The full set of results is compiled in Figure 9 where the three remaining points were also plotted.

A final remark concerning Figure 9 is pertinent at this point. In the figure, we have introduced some error bars that are particularly relevant for the benzene molecules with higher degrees of fluorine substitution. These error bars reflect the experimentally observed temperature dependence of the solubility limits of those molecules in the ionic liquid: solubility decreases as temperature increases.^{2,3} For 1,2,4-trifluorobenzene, this change is particularly striking, with the two components of the mixture showing complete miscibility at temperatures around 300 K, a lower critical solution point ($T_{\text{LCST}} = 355 \text{ K}$; $x_{\text{LCST}}(\text{C}_6\text{H}_3\text{F}_3) = 0.95$), and therefore phase separation above

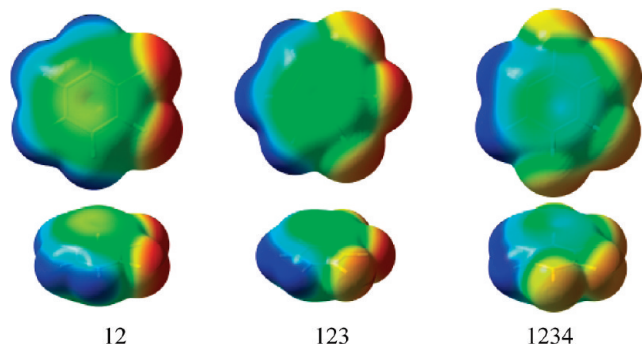


Figure 7. Charge distributions around the three aromatic molecules with larger dipole moment (above $9 \times 10^{-30} \text{ C}\cdot\text{m}$). From left to right: 1,2-difluorobenzene, 1,2,3-trifluorobenzene, and 1,2,3,4-tetrafluorobenzene. Top row: frontal views of the aromatic molecules with all dipole moments pointing to the right. The x -, y -, and z -axes are oriented horizontal, vertical, and normal to the sheet directions, respectively. Bottom row: side views of the molecules with the z -axis oriented in an almost vertical direction. Positively or negatively charged areas are indicated by color gradients changing from dark blue to red, respectively.

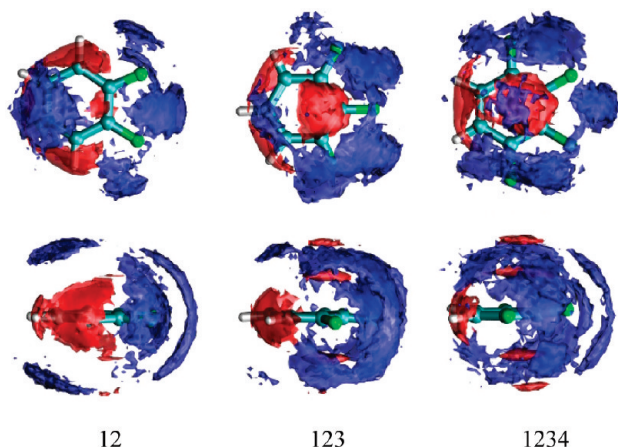


Figure 8. Spatial distribution functions of $[\text{C}_2\text{mim}][\text{NTf}_2]$ around the three aromatic molecules with larger dipole moments. The nature and orientation of the three aromatic molecules are the same as those presented in Figure 7. The color coding is also the same as in Figure 6.

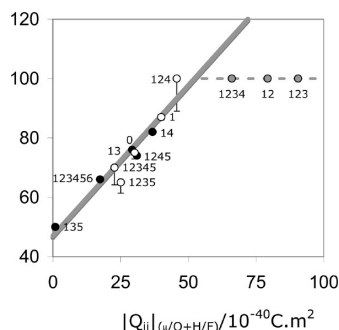


Figure 9. Correlations between the solubility in $[\text{C}_2\text{mim}][\text{NTf}_2]$ of benzene and its 12 fluorine-substituted derivatives and their relevant quadrupole moment moduli corrected for the effect of the dipole moment and the difference between anion–hydrogen and cation–fluorine interactions. The gray line corresponds to eq 1.

that temperature (Figure 4b or ref 3). These entropy driven situations are rarely found, with only a few reported cases for systems containing ionic liquids.^{22,23}

The present correlation was performed using solubility data at 300 K and could have been modified to incorporate those temperature dependences. However, it is our contention that

more important than any possible modification of the empirical correlation is the interpretation at a molecular level of the difference between the solubility of the hydrogenated and fluorinated molecules in the ionic liquid (almost no temperature dependence in the former, a decrease with increasing temperature in the latter). As we have noticed earlier, the different SDFs of Figures 3, 6, and 8 show that the interactions between the anions and the hydrogen atoms of the aromatic molecules are much more localized (suggesting the existence of hydrogen bonding) than the cation–fluorine atom counterparts. As temperature increases, these more localized interactions will tend to break apart and the solubility of the aromatic molecules in the ionic liquid will decrease. The larger temperature-related shift of solubility in pentafluorobenzene (where there is only one anion–hydrogen interaction) when compared to that in hexafluorobenzene (with no such interactions) or in benzene (where there are six such interactions but that are delocalized around the equator of the aromatic molecule) are a likely consequence of that.

4. Conclusions

The effect of the dipole and quadrupole moments on the solubility of fluorinated benzenes in $[\text{C}_2\text{mim}][\text{NTf}_2]$ was interpreted by investigating the structure of the solvation sphere of ions around the aromatic molecules. As expected in an ionic medium, the distribution of solvent ions closely follows the electrostatic charge distribution in the solute molecules.

Three main insights were formulated when trying to correlate the solubility and miscibility data of the entire family of benzene plus its 12 fluorinated derivatives in the ionic liquid $[\text{C}_2\text{mim}][\text{NTf}_2]$, and the calculated multipole moments of the aromatic molecules.

First, it is the (absolute value of the) largest component of the principal-axes quadrupole moment that controls the solubility in the first approximation, and not necessarily the component of the quadrupole moment corresponding to the π -electron cloud in the aromatic solute.

Second, it was observed that differences in the interactions of the hydrogen and fluorine atoms of the aromatic molecule with the ionic liquid have consequences on the solubility and on the structure of the solutions. The interaction of H atoms of the solutes is stronger and more localized with sites of negative charge (the O atoms) on the NTf_2^- anions than the interactions of F atoms of the fluorobenzenes with the imidazolium groups of the cations. The effect is transferable across the entire family of fluorinated benzenes and can be captured by just one parameter.

Third, when both dipole and quadrupole moments are present in the solute, they have an antagonistic effect, reducing the solubility in the ionic liquid. This is understood by looking at the destructuring of the arrangement of ions around the aromatic molecules that possess both non-negligible dipole and quadrupole moments. Again, this dipole/quadrupole interference across the entire set of fluorinated benzenes can be captured by just one more parameter.

An initially difficult to understand situation regarding the solubility and miscibility of the 13 aromatic compounds in an ionic liquid has been reduced to a simple linear correlation, through the analysis of the effects of the different components of the quadrupole and of the dipole moment. The ionic liquid in question offers a relatively simple solvation environment, since it does not contain a sufficiently long alkyl side chain to give rise to segregation between nonpolar and charged domains in the pure liquid.¹ In ionic liquids with longer side chains, the

structure of the solutions is expected to be more complex, but given the ionic nature of the solvent, for dipolar and quadrupolar solutes the dominant factor will still be the electrostatic interactions. Therefore, we anticipate that the conclusions drawn herein contribute to a general understanding of the solvation of compounds with different degrees of polarity in ionic liquids.

We would like to stress that the present simulations were performed to illustrate at a molecular level the structure of ionic liquid solutions of the different aromatic solutes, i.e., the distribution of anions and cations around a given benzene derivative. As such, the simulations were performed at low concentrations of benzene so that the solute–solute interactions would not perturb an already complex situation. Other simulations (with larger concentrations of solute) aiming at the volumetric or energetic properties of this kind of mixture are also possible but, in our opinion, lie outside the scope of the present paper. Further work in that direction is both welcome and useful. The same applies to the difficult task of predicting by simulation techniques the solubility of these solutes in a given ionic liquid.

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Supporting Information Available: Tables showing the full set of parameters for benzene and its derivatives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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