Quantum Chemical Studies on the Simultaneous Interaction of Thiophene and Pyridine with Ionic Liquid

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The simultaneous interaction of thiophene and pyridine with different ionic liquids:1-butyl-1-methylpyrrolidinium tetrafluoroborate([BPYRO][BF_4]),1-butyl-1-methylpyrrolidinium hexafluoro-phosphate ([BPYRO][PF_6]), 1-butyl-4-methylpyridinium tetrafluoroborate ([BPY][BF_4]), 1-butyl-4-methylpyridinium hexafluorophosphate ([BPY][PF_6]) and 1-benzyl-3-methylimidazolium tetrafluoroborate ([BeMIM][BF_4]) were investigated using quantum chemical calculations. A three-tier approach comprising of partial charges, interaction energies and sigma profile generation using conductor-like screening model for real solvents (COSMO-RS) was chosen to study the systems. A quantitative attempt based on the CH-π interaction in ionic liquid; thiophene–pyridine complexes gave the interaction energies of ILs in the order: [BPY][BF_4] > [BPYRO][PF_6] > [BeMIM][BF_4] > [BPY][PF_6] > [BPYRO][BF_4]. An inverse relation was observed between the activity coefficient at infinite dilution predicted via COSMO-RS–based model and interaction energies. The dominance of CH-π interaction was evident from the sigma profiles of ionic liquid together with thiophene and pyridine. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 749–764, 2011

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Introduction

By 2010, our petroleum industry is bound to produce ultralow sulfur diesel (ULSD) containing a maximum of 15 ppm sulfur.[1,2] The simultaneous removal of aromatic compounds of nitrogen and sulfur from diesel oil is becoming increasingly difficult because of its resistance to hydrodesulfurization (HDS).[3] Ionic liquids (ILs) better known as green solvents provide an important alternative in removing such compounds by liquid–liquid extraction. It is likely that diesel containing 50 ppm sulfur will have to be produced in India in the near future.

HDS requires high-energy consumption and investment cost because of reactor, vessel, and pumps. When diesel is desulfurized at higher pressure, many olefins are saturated resulting in lowered octane numbers. Higher temperature processing also leads to increased coke formation and subsequent catalyst deactivation. The reactivity of organosulfur compounds over HDS catalysts depends on the molecular structures of sulfur-containing compounds. The aliphatic organosulfur compounds like thiols (R-SH), thioethers (R-S-R), and disulphides (R-S-S-R) are very reactive in conventional hydroprocessing and they can be completely removed from the fuels without much difficulty. The aromatic sulfur compounds including thiophenes (TS), benzothiophenes, and their alkylated derivatives are generally more difficult to convert over hydroprocessing catalysts. Therefore, the aromatic sulfur compounds present the most difficult challenges

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to the HDS processes. The nitrogen compounds such as six-membered ones like pyridine (PY), quinoline, isoquinoline, and the five-membered ones such as pyrrole, indoles are usually present in diesel oil. It was observed that the nitrogen compounds in the refinery streams are known to inhibit the hydrodesulfurization reaction.[4]

ILs are attractive solvents for desulfurization and denitrification and are competitive with respect to molecular solvents in the following ways: (a) environmentally benign and designable; (b) nonvolatile, nonflammable, highly solvating, and noncoordinating medium having a high thermal stability over a wide liquid range; (c) higher sulfur extracting ability and virtually immiscibility with diesel, preventing cross contamination; and (d) recovery and regeneration involving simple heating to recover the sulfur compounds intact. The interest in ILs is due to many possible combinations of cations and anions, allowing the fine-tuning of their density, viscosity, melting point, hydrophobicity, and, most importantly, their solvent power. ILs such as 1-octyl-3-methylimidazolium bis-trifluoro methylsulfonylimide [OMIM][TFI][5,6] and 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF_4][7] have been tested for the extraction of TS from aliphatic hydrocarbons with encouraging results. ILs such as 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] showed there was little absorption for paraffins and olefins, but a high ratio of TS/aromatics was obtained in the IL rich phase.[8] ILs such as 1-alkyl-3-methylimidazolium tetrafluoroborate [RMIM] [BF_4],1-alkyl-3-methylimidazolium hexafluorophosphate [RMIM] [BF_4], and trimethylamine hydrochloride ($AlCl_3$-TMAC) showed high selectivity, particularly toward aromatic sulfur and nitrogen compounds.[9] Phosphoric-based ILs such as 1-methyl-3 methylimidazolium dimethylphosphate [MMIM] [DMP], 1-ethyl-3-methylimidazolium diethyl phosphate [EMIM][DEP], and 1-butyl-3-methylimidazolium dibutyl phosphate [BMIM][DBP] were found to extract sulfur components such as 3-methylthiophene(3-MT), benzothiophene(BT), and dibenzothiophene(DBT). Further sulfur partitioning coefficient (k_n) i.e., amount of sulfur in ionic liquid phase to the amount of sulfur in diesel oil was measured for [BMIM] [DBP], [EMIM][DEP], and [MMIM][DMP].[10]

In recent years, theoretical quantum chemical calculations have become complementarities for experimental methods in many fields.[11–15] Recently, we have used quantum chemical based COSMO-RS predictions for evaluating the performance of 264 possible cation–anion pairs in the removal of TS from diesel oil.[16] As the aromatic sulfur and nitrogen compounds are present together in the diesel oil, a need was felt to study its interaction with different classes of ILs. The goal of this work is to apply quantum chemical calculations to investigate the fundamental nature of those systems and the development of a methodology that allows the prediction at molecular and atomic level. This would be very valuable for the design of the particular IL, which is most suitable for the simultaneous removal of TS and PY from diesel oil. Till date, only one such study by Zhang et al.[17] has been carried out to study the interaction of TS with two ILs: [BMIM] [BF_4] and [BMIM][PF_6]. The unusually high solubility of aromatic compounds in ILs in comparison with aliphatic compounds has been explained by electrostatic interactions between the cations and the π-system of the aromatic compounds[18] and by the formation of liquid clathrates.[19]

Till date, the nature of the interactions between the π-system of the aromatic compounds and the charged ions of the ILs has been suggested but not experimentally demonstrated. The present study is the first attempt to study the simultaneous removal of both PY and TS on a quantum chemical scale. Further for the first time, the effect of other cations namely the pyridinium, pyrrolidinium, and benzylimidazolium have also been taken up.

Computational details

MOLDEN[20] visualization package have been used to prepare the initial structures. Dummy atoms have been used for complexes such as ILs where the cation and anion are initially connected together using a dummy atom. When the molecule/complex is geometrically optimized; the final result has a structure without the dummy atom. This concept has been used earlier by Meng et al.[21] and Turner et al.[22] for ab initio calculations on ILs. In a similar manner, complexes or cluster linking ionic liquid with PY and TS were also prepared.

The density functional theory of Becke's three parameter exact exchange functional together with the gradient corrected correlation functional of Lee, Yang, and Parr represented as B3LYP[23] were used to compute the optimized geometry using the 6-311+G* basis set. The calculations were performed by Gaussian 03 program.[24] After a successful completion of an optimization job, vibrational analysis (frequency calculation) was used to determine the nature of stationary points found by a geometry optimization.[25] Absence of imaginary or negative frequencies indicated that the structure is a global minimum. Thereafter, the partial charges were estimated on the optimized geometry using the CHELPG[26] scheme as given in Gaussian 03. The many body analysis[27] were performed for the simultaneous removal of complexes consisting of TS and PY, and the calculation of the interaction energy was done by the following expression:

$$\mathrm{IE} = E_{\mathrm{IL+PY+TS}} - (E_{\mathrm{IL}} + E_{\mathrm{PY}} + E_{\mathrm{TS}})$$

where IE is the interaction energy [ILs, TS, PY] of the whole complex in kJ/mol; $E_{\mathrm{IL+PY+TS}}$ is the total energies for the complex system in kJ/mol; and E_{IL}, E_{PY}, and E_{TS} are the individual energies of the ILs, TS, and PY, respectively, in kJ/mol.

The conductor-like screening model (COSMO) has been described in the work by Klamt.[28] In conductor-like screening model for real solvents (COSMO-RS), molecules are treated as a collection of surface segments.[29] An expression for the chemical potential of segment in the condensed phase is derived in which interaction energies between segments are calculated from COSMO-RS. The chemical potential of each molecule is then obtained by summing the contributions of the segments. The extension to RS is given in an excellent work of Klamt et al.[30,31] and Sandler et al.[32] COSMO-RS model has been successfully applied to various domains of ILs in the past. A recent review on the property prediction of ionic liquid mixtures by COSMO-RS model has been given by Klamt et al.[33] The application of COSMO-RS to Ionic Liquid mixtures have been undertaken by various authors recently. Freire et al.[34] have studied the liquid–liquid equilibrium (LLE) and vapor–liquid equilibrium (VLE) for several combinations of ILs with alcohols using COSMO-RS model. The same authors evaluated and predicted the LLE and VLE of aqueous systems of ILs using COSMO-RS model.[35] Further, binary LLE system of IL with ethanol, 1-propanol, and 1-butanol were investigated over the whole molefraction of ionic liquid at ambient pressure by Sahandzhieva et al.[36] COSMO-RS model have also been applied successfully for the screening of potential ionic liquid for the separation of 1-hexene and *n*-hexane[37] mixtures. LLE of ionic liquid (1-alkyl-3-methylimidazolium methylsulphate) with alcohols, ethers, and ketones have been predicted using COSMO-RS model by Domanska et al.[38] They also predicted the binary LLE for the IL system namely 1,3-dimethylimidazolium or 1-butyl-3-methylimidazolium methylsulfate with hydrocarbons such as benzene, toluene, ethyl benzene, propylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene at atmospheric pressure.[39] In our earlier work, COSMO-RS model have successfully used for the prediction of binary VLE[40] and ternary LLE[41,42] of imidazolium based ionic liquid. Additionally, infinite dilution activity coefficients (IDAC) values of solutes in ILs were successfully predicted by Klamt et al.[43] and Banerjee et al.[44] The expression and methodology are given in details in our previously published work on COSMO-RS model.[40–42,44]

The quantum chemistry package of Gaussian 03[24] has been used to compute the COSMO files. The first step for COSMO-RS calculation is to estimate the sigma profile of each species. The equilibrium geometry of the cations and anions in the ideal gas phase are first obtained separately using the density functional theory of PBV86[45] along with triple zeta valence potential (TZVP)[46] basis set in combination with the density fitting basis set of DGA1.[47] The ideal screening charges on the molecular surface are then computed using the same level of theory [P BV86]. The radii of the elements are used to define the cavity for the molecule. For phosphorous, a default value of 1.17 R_{Bondii}[48,49] has been used.

Results and Discussion

On a quantum scale the interactions of IL-TS/PY depend on the π–π interaction, CH–π interaction, and the hydrogen bonding interactions.[11] π–π interactions act strongly on flat polycyclic aromatic hydrocarbons such as anthracene, triphenylene, and coronene because of the presence of many delocalized π-electrons. A recent work carried out on a double concave hydrocarbon buckycatcher[50] had an association constant of 8600 M^{-1}. This interaction, which is stronger than other noncovalent interactions (hydrogen bonds, van der Waals forces, etc) plays an important role.

Cation–π interaction energies are of the same order of magnitude as hydrogen bonds and play an important role in molecular recognition.[51] This interaction, known as "π–cation interaction," plays a dominant role in both chemical and biological recognition.[52] π–cation interaction has been experimentally evidenced by mass spectrometry and NMR spectroscopy.[53–55] Smaller and more positively charged cations lead to larger electrostatic attraction. The electronic properties of the substituents on the π system also have an influence on the strength of the attraction. Electron withdrawing groups decrease the amount of negative charge in the π system and thus weaken the interaction while electron donating groups such as $-NH_2$ increase the amount of negative charge in the π system. Thus the partial charge on the nitrogen/sulfur atom of PY/TS will play an important role in increasing or decreasing the negative charge in the π system.

Often the molecular structure orientation is involved in the separation of organic /inorganic compounds through multiple interactions by CH—π bond.[56] The CH—π bond is strongly responsible for the simultaneous interaction by tuning the donor and acceptor ligand properties of the interacting molecules.[57] Though the CH—π bond is weak, still it is known to lie within the lower end of the hydrogen bonding regime.[58] The electron withdrawing tendency of CH carbon and electron donating tendency of π aromatic system are known to play a significant role in multiple interactions.[57] Suezawa et al.[56] studied the importance and effectiveness of the aromatic CH–π hydrogen bond for complex cluster formation. Moreover, the aromatic ring current in TS is stronger than that of ionic liquid. This is due to the fact that the bulky anions such as PF_6 prevent BMIM cation to come close and thus reduces its aromatic current effect.[59] The TS molecules are tightly packed giving rise to high aromatic current density. Because of this the π–π interaction between cation and TS/PY is greatly reduced and the CH–π interaction takes over. In a recent work by Cassol et al.,[60] the high affinity of the IL for aromatics (with and without sulfur), were experimentally found to be due to CH–π interactions between the hydrogens of the IL ring and those of the aromatic compounds. The above study implies that the CH–π bond plays a considerable role within the π group of TS /PY and CH group of ILs. The hydrogen bonding effect due to the H-bond donor of cation to the sulfur/nitrogen atom of TS/PY will be taken up later using COSMO theory.

Effect of partial charges

Recent studies[17,61,62] showed that the normal bonded orbital (NBO) analysis is used as an excellent tool for the investigation of partial charge transfer interaction within the parent compounds. Further, the chemical reactivity is also explained on the basis of the partial charges.[63,64] Based on these partial charges, difference in the hydrogen-bonding, electrostatic interaction, and CH–π bonding interaction is considered. Therefore, based on the quantum chemical investigation, the CH groups can participate and play an important role in the simultaneous interaction of π bases compounds such as TS and PY.[60]

Table 1 shows the number of stable sites (i.e., hydrogen atom) having positive charges on the cation. The number of "+ve" charged hydrogen atom increases from [BPYRO] (19) $>$ [BPY] (16) $>$ [BeMIM] (13). It should be noted that the rear hydrogen atoms of the cation are unlikely to form CH–π interaction with TS/ PY.[17,65] The two H-atom of

Table 1. The H-bond Donor /Acceptor of Different Cations

S. No	Objective	[BPYRO]	[BPY]	[BeMIM]
1	An available H-bond donor/ acceptor of cation to sulfur and nitrogen	H 0.059221	H 0.172946	H 0.152042
		H 0.058873	H 0.129888	H 0.209860
		H 0.061347	H 0.129239	H 0.207561
		H 0.086002	H 0.129084	H 0.123234
		H 0.114472	H 0.172899	H 0.121577
		H 0.111414	H 0.173994	H 0.121796
		H 0.018728	H 0.133369	H 0.109687
		H 0.004660	H 0.176477	H 0.119711
		H −0.006327	H 0.134885	H 0.117665
		H 0.007086	H −0.020758	H 0.119809
		H 0.081874	H −0.021695	H 0.127274
		H 0.049630	H −0.022032	H 0.130990
		H 0.038720	H −0.022610	H 0.128220
		H 0.064410	H 0.093133	
		H 0.080052	H 0.070041	
		H 0.157920	H 0.070294	
		H 0.163081		
		H 0.169325		
		H 0.037685		
		H 0.087232		
2	Number of positive sites available	19	16	13
3	Number of negative sites available	01	Nil	Nil

"CH_2" group cannot be occupied at the same time due to columbic repulsion. Thus, there is a limit on the maximum number of site that can be occupied at a time. The electrostatic field effect within the IL is also important when electrons surrounding the resonating nucleus of the cation are displaced with a chemical bonded polar atom such as fluorine (F–H interaction), which is present in both anions. An individual cation or anion does not give much information about the interaction of IL with TS/PY. For favorable interaction the pryridine/TS molecule should be able to overcome the F–H interaction and form cation—π or hydrogen bonds. In our further discussion, we will focus our attention on the partial charge of nitrogen and sulfur atom when they are in a complex consisting of ionic liquid. The partial charge of sulfur atom in TS is −0.06.[17] The "electron pairs" on sulfur atom are significantly delocalized in the π electron system. The nitrogen atom on PY having a partial charge of −0.679 (Figure 1) can act as a basic lone pair of electrons. As this lone pair is not delocalized into the aromatic π-system, it is therefore basic in nature. For efficient CH–π interaction, the aromatic π density needs to increased. A decrease in the partial charge of nitrogen or sulfur atom will result in the increase in the density of the π system thereby promoting cation–π interaction.

Pyrolidinium-based ionic liquid

Table 2 presents the partial charges derived for sulfur and nitrogen in various complexes. The partial charge of sulfur (−0.0137) in $[BPYRO][BF_4]$ + TS complex is less than that of $[BPYRO][BF_4]$-TS-PY (−0.037). Thus CH–π bond interaction will be weaker for the simultaneous removal when compared with the removal of TS alone. For the case of PY the partial charge decreases from −0.681($[BPYRO][BF_4]$-PY) to −0.382($[BPYRO][BF_4]$-PY-TS) indicating stronger CH–π interaction for simultaneous removal. Thus, for the simultaneous removal, TS and PY does not compete for the same site within the ionic liquid ($[BPYRO][BF_4]$) as the partial charges of either nitrogen (−0.679) or sulfur (−0.06) atom is less than that obtained in complex form. The aromatic current effects in PY and TS will be stronger and thus they will be able to form CH—π bonds. For $[BPYRO][PF_6]$, a similar effect was observed. The partial charge of sulfur (0.1631) in $[BPYRO][PF_6]$-TS complex is positive as compared to $[BPYRO][BF_4]$-TS-PY (−0.035). It indicates that the CH-π bond formation is not favorable in $[BPYRO][PF_6]$-TS complex. For the case of PY the partial charge on nitrogen reduces from −0.697 ($[BPYRO][PF_6]$-PY) to −0.391 ($[BPYRO][PF_6]$-PY-TS), which is again less than that of either nitrogen (−0.679) or sulfur(−0.06) atom indicating strong simultaneous removal. However for $[BPYRO][PF_6]$-PY CH–π is not favorable as its partial charge of nitrogen (−0.697) is greater than −0.679 indicating less delocalization.

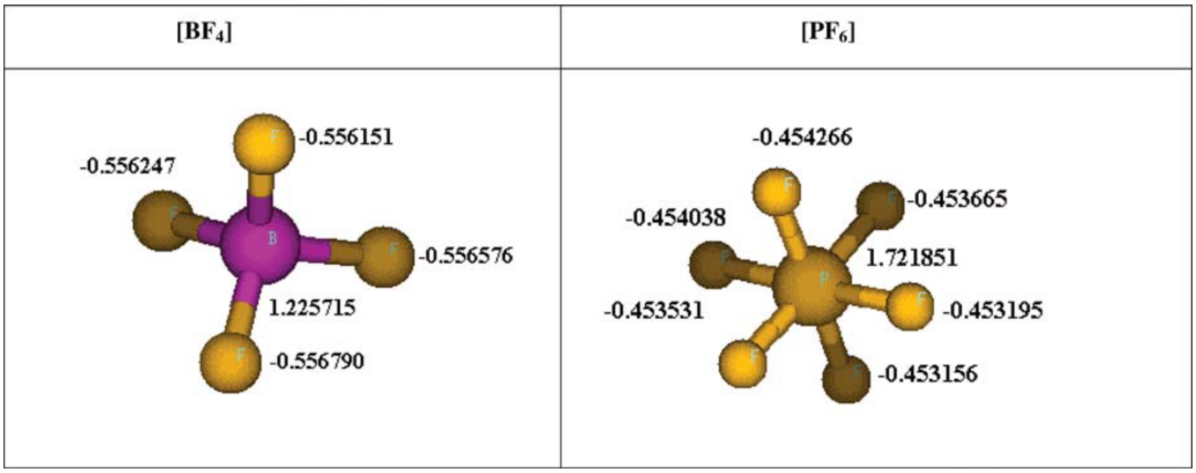


Figure 1. Optimized geometries of Anions ($[BF_4]$ and $[PF_6]$).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. The Partial Charge of Sulfur and Nitrogen on Complexes Involving Ionic Liquids

S. No.	Name of the System/Complex	[BPYRO][BF$_4$]		[BPYRO][PF$_6$]		[BPY][BF$_4$]		[BPY][PF$_6$]		[BeMIM][BF$_4$]	
		S	N	S	N	S	N	S	N	S	N
1	Thiophene	−0.0136	Nil	0.161	Nil	0.091	Nil	−0.029	Nil	−0.02355	Nil
2	pyridine	Nil	−0.68063	Nil	−0.69785	Nil	−0.6809	Nil	−0.68766	Nil	−0.37886
3	Thiophene + pyridine	−0.03659	−0.382102	−0.03505	−0.39108	−0.03489	−0.43567	−0.02714	−0.34085	−0.027697	−0.46125

Partial charge on sulfur atom: −0.06[17]; partial charge on nitrogen atom: −0.679 (Figure 3).

Pyridinium-based ionic liquid

For [BPY][BF$_4$] the partial charge on nitrogen decreases from −0.6809 ([BPY][BF$_4$]-PY) to −0.435 ([BPY][BF$_4$]-PY-TS) while for TS the partial charge on sulfur increases from +0.091 ([BPY][BF$_4$]-TS) to −0.0348 ([BPY][BF$_4$]-PY-TS) thus improving the CH-π interaction when they are considered simultaneously. It indicates that [BPY][BF$_4$] cannot be a good solvent for the removal of TS or PY individually. The trend was similar for [BPY][PF$_6$] where the partial charge on nitrogen decreased from −0.687 ([BPY][PF$_6$]-PY) to −0.348 ([BPY][PF$_6$]-PY-TS) while for TS the partial charge on sulfur remained stationary ~-0.029 for both complexes ([BPYR][PF$_6$]-TS and ([BPYR][PF$_6$]-PY-TS).

Benzylimidazolium-based ionic liquid

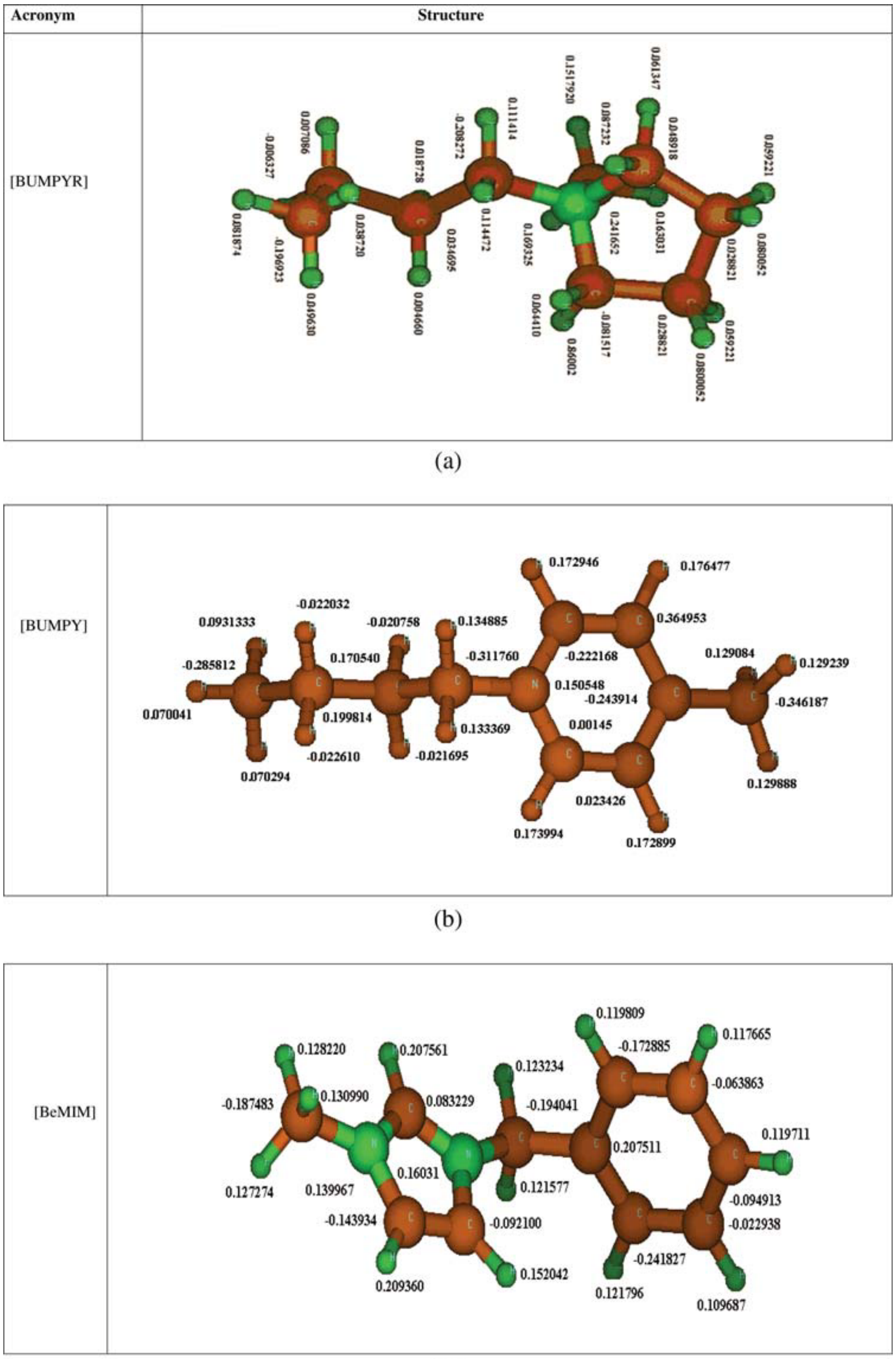
The CH–π bonds interactions are seen to be dominant for both [BeMIM][BF$_4$]-TS and [BeMIM][BF$_4$]-PY complex. For the case of PY the partial charge on nitrogen increases from −0.3788([BeMIM][BF$_4$]-PY) to −0.461([BeMIM][BF$_4$]-PY-TS) while for TS the partial charge on sulfur increases from −0.023 ([BeMIM][BF$_4$]-TS) to −0.027 ([BeMIM][BF$_4$]-PY-TS). For the simultaneous removal, the partial charges of nitrogen decreases from −0.679 to −0.461 while for sulfur it decreases from −0.06 to −0.027 indicating greater aromatic π density in TSTS and PY respectively. It can be seen that the partial charges of nitrogen and sulfur in all the ILs for the simultaneous complex is less than the partial charge of nitrogen (−0.679) and sulfur (−0.06) in TS and PY, respectively. This indicates all the ILs have a favorable CH-π interaction with both TS and PY.

Effect of Interaction Energies

In this section, interaction of TS/PY with cation, anion, and IL (cation + anion) have been studied explicitly and simultaneously. Figures 1 and 2 shows the optimized structures of anions and cations, respectively, while Figure 3 shows the optimized structure of PY and TS. The optimized structure of TS has been referred form previous work.[17] Figure 4 presents the optimization results for two anions ([PF$_6$] and [BF$_4$]) and three cations ([BPYRO], [BPY], and [BeMIM]) and their interaction with TS. Both anions i.e., [BF$_4$] and [PF$_6$] are situated outside the ring plane of TS, respectively, and the fluorine atoms were found to interact with the hydrogen atoms of the TS through F–H interaction. This shows that the F–H interaction is important in the system. Such structure produces a maximal Columbian effect[28] with the same charge repelling each other and the opposite charges attracting each other. In the case of the octahedral [PF$_6$] anion, the equatorial flourine atoms participate preferentially in hydrogen bond network, whereas for tetrahedral [BF$_4$] anions only three of the atoms are usually involved in the linkage. This reasonably agrees with the prediction of Zhang et al.[17] For the cations, the optimized structure were obtained using the same procedure as outlined by Zhang et al.[17] The optimized structure indicates that the TS is located aside the aromatic ring of the cation with its aromatic ring being perpendicular to the aromatic ring of the cation. With this structure, the positively charged atoms of the [BPYRO], [BPY], and [BeMIM] cations are the most approachable by the negatively charged atoms of TS, producing a maximal columbian attraction. This agrees well with the partial charges giving the number of stable hydrogen sites (Table 1) in the cations. These strongest hydrogen bond always involves the most acidic hydrogen of [BPYRO], [BPY], and [BeMIM] based cation followed by the other hydrogens of the [BPYRO], [BPY], and [BeMIM] nucleus and/ or the hydrogens of the *N*-alkyl radicals. These bonds possess properties of weak to moderate hydrogen bonds and are mostly electrostatic in nature. The H—F bond lengths were found to be greater than 2.2 Å; while the C—H···F bond angles were between 100° and 180°. It should be noted that the origin of long-range cation liquid crystalline properties[35] is due to the formation of domain of ‘‘coulombic layers.’’ The cationic head groups (i.e., alkyl group) interact with the counter ions, and the ‘‘van der Waals’’ layers built from (anti) parallel stacking of the alkyl chains.

Figure 5 shows the optimized geometry of two anions ([PF$_6$] and [BF$_4$]) and three cations based ([BPYRO], [BPY], and [BeMIM]) and their interaction with PY. Both anions i.e. [BF$_4$] and [PF$_6$] are situated outside the ring plane of the PY, and the fluorine atoms interact with the hydrogen atoms of the PY. Such structure again produces a maximal Columbian effect with the same charge repelling each other and the opposite charges attracting each other. For the cations, the interaction was found to be preferentially through N (heteroaromatic)—H (imidazolium) hydrogen bonds. Previous work suggests that this is largely controlled by the nitrogen heterocyclic pK_a value.[60] It is clear that interaction of PY with the cations increases the π density as the partial charge of nitrogen on PY molecule (Figure 3) decreases from −0.679 to −0.307 and −0.297 while interacting with [BeMIM] and [BPY] respectively, while it remains constant with [BeMIM] i.e., −0.684.

The optimized energies between TS with ILs are given in Table 3. The interaction of TS with the different ILs is preferentially through CH—π bonds and the quantity of TS



(a)

(b)

(c)

Figure 2. Optimized geometries of Cations ([BPYRO] [BPY] [BeMIM]).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with ionic liquid pair increases with the increase of the π-density.[4] Based on their interaction energies the ILs follow the order: [BeMIM][BF_4] > [BPYRO][BF_4] > [BPY][BF_4] > [BPY][PF_6] > [BPYRO][PF_6] (Table 3). It should be noted that negative interaction energy is favorable since it means extra amount of energy (positive in nature) is required for disassembling the system/complex. It can be seen that there is a qualitative relation between the partial charges and interaction energies. [BPYRO][PF_6]-TS complex having interaction energy of +25.30 kJ/mol has a

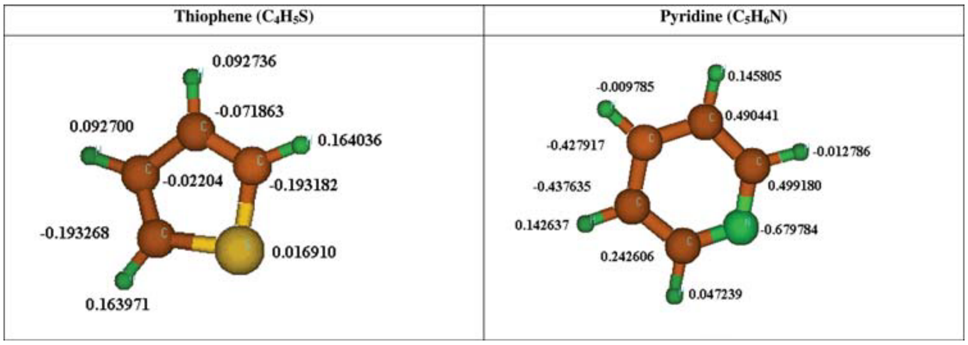


Figure 3. Optimized geometry of thiophene and pyridine.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

partial charge of +0.161 on the sulfur atom. The positive sign of partial charge is contrary of what was observed for sulfur in TS alone (i.e., −0.06). The positive charge results in very less delocalization and ultimately leads to a positive value of interaction energy. In the same manner [BPY][BF_4]-TS complex having interaction energy of 10.53 kJ/mol has a partial charge of 0.091 on the sulfur atom contrary to the partial charge of sulfur in TS (−0.06). The optimized energies of the IL with PY are given in Table 3. The interaction of PY with the different ILs again occurs through N (heteroaromatic)—H (cation) hydrogen bonds as previously reported.[50] The interaction energies followed the order: [BPY][PF_6] >[BeMIM][BF_4] > [BPYRO][BF_4] > [BPY][BF_4] > [BPYRO][PF_6] (Table 3). For [BPYRO][PF_6]-PY complex the positive interaction energy (88.40 kJ/mol) is due to the partial charge of nitrogen, which is −0.697. This is more than the partial charge of nitrogen in PY alone (−0.679). This leads to lesser delocalization and subsequently less aromatic π density in the PY molecule.

Figure 6 shows the optimized geometry of ionic liquid-TS-PY complex along with their partial charges. It is seen that the interaction is mainly through cation-TS-PY contacts (CH—π bond). Based on the interaction energies the degree of extraction follows the order [BPY][BF_4] > [BPYRO][PF_6] > [BeMIM][BF_4] > [BPY][PF_6] > [BPYRO][BF_4]. The result is contrary of what was obtained for IL-TS/PY. However the variation in interaction energies are very small i.e., −23.39 KJ/mole [BPYRO][BF_4] to −48.50 KJ/mole [BPY][BF_4] (Table 3).

IDAC Predictions

Till now, we have discussed the interaction energies which cannot be measured experimentally. However, an attempt is made where the interactions energies can be correlated to experimental measurements. The most challenging and difficult part are in removing the last traces of PY/TS species from diesel oil. The IDAC is an important indicator which quantifies this very phenomenon. Further, the activity coefficient at infinite dilution can be measured via gas–liquid chromatography and gives us an important descriptor for the effectiveness of a solvent to remove the last trace of impurity (i.e., TS or PY in our case). Lesser the IDAC values from unity, greater is the tendency for the ionic liquid to remove nitrogen/sulfur species. We have successfully compared the IDAC in our previous work[44] for ILs. Thus we have predicted the IDAC values of PY and TS in ILs (Table 3) which can be treated as close to experimental values and serve as a test for our computational chemistry basis. For the prediction of IDAC values, we have used the COSMO-RS parameters as reported in our previous work.[40] It can be seen from Table 3 that interaction energies of PY are higher than that of TS. However, the activity coefficient at infinite dilution of PY is lower than that of TS. Thus, an inverse relation between activity coefficient at infinite dilution and interaction energies is obtained. Smaller values of interaction energies indicate higher activity coefficient thereby lesser solubility with the solvent.

The only anamoly in this complex is the one with the complex: [BPYRO][PF_6]-TS and [BPYRO][PF_6]-PY. The interaction energies are positive in this case as the IL is solid at room temperature. The positive interaction energies imply that the columbic interactions are very high as compared to π–π interaction.

Effect of Sigma Profile

In the COSMO scheme, sigma profile is the only descriptor, which describes the local polarity of molecular surface and determines the interaction energies, replacing the empirical interaction parameters usually used in chemical engineering models like UNIQUAC and UNIFAC. This further shows the polarity of the components in a mixture or within itself. The most important descriptor used in sigma profile is the local screening charge density σ, which would be induced on the molecular surface if the molecule would be embedded in a virtual conductor. This descriptor, which can be calculated at reasonable cost by quantum chemical programs using the continuum solvation model COSMO,[28] is an extremely valuable tool for the local polarity of molecular surface. This single-molecule ideal solvation calculation needs to be done only once for each molecule, regardless of the mixture in which the molecule appears. The screening charge density σ is the only descriptor determining the interaction energies. Thus, the ensemble of surface pieces characterizing a pure compound (or a mixture S) is sufficiently described by the distribution function p_S (σ), which describes the relative amount of surface in the ensemble having a screening charge density between σ and $\sigma + d\sigma$. The

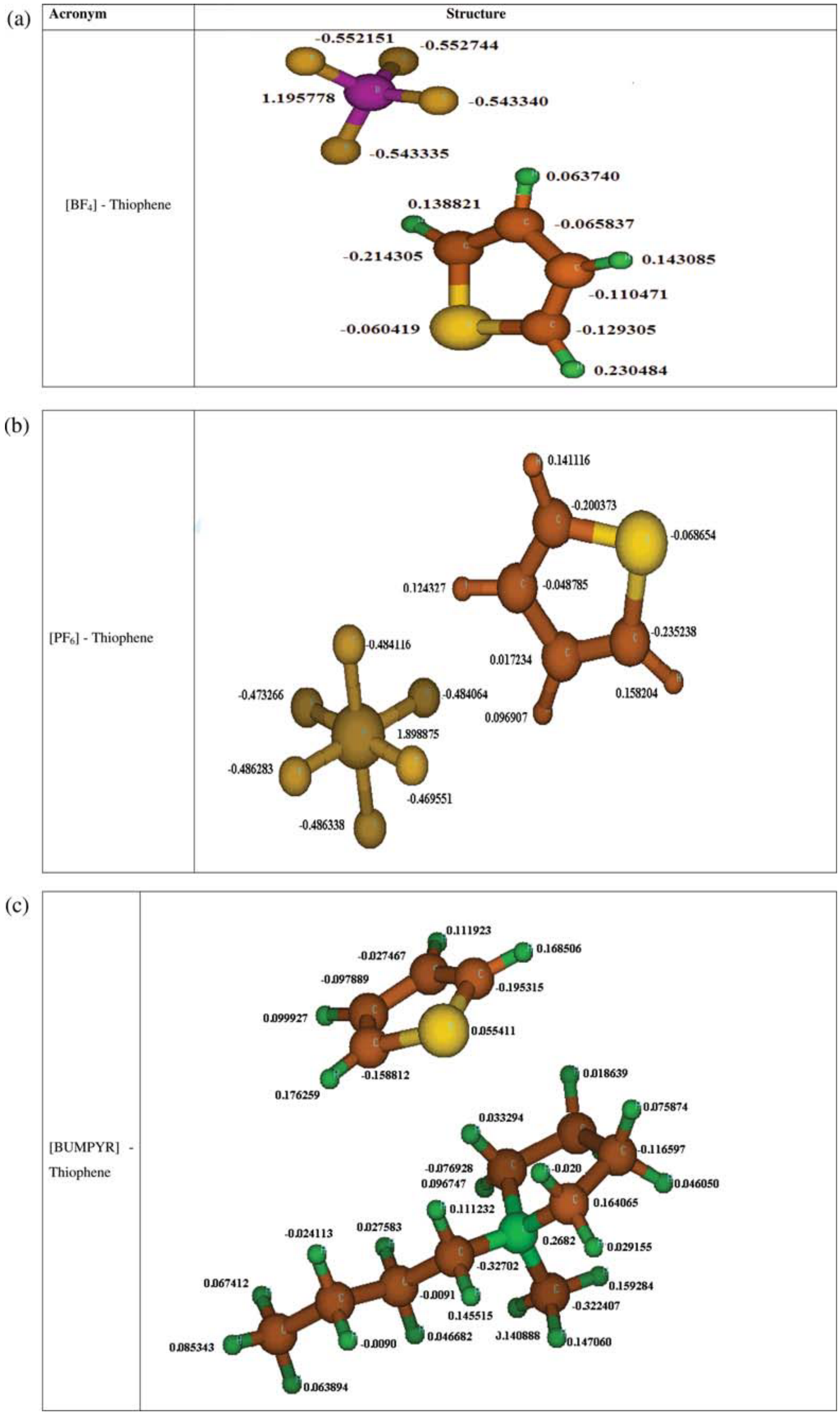


Figure 4. Optimized geometries of cations and anions with thiophene.

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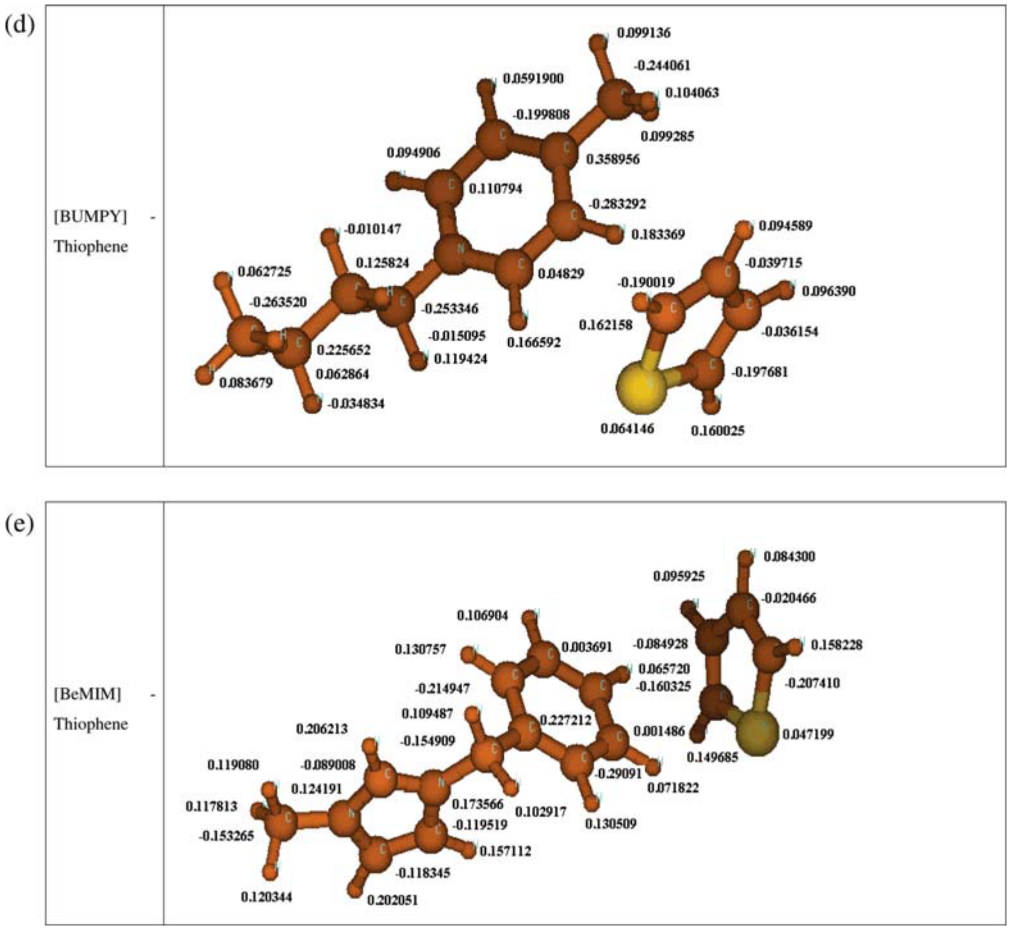

Figure 4. (Continued)

notation "σ-profile" is used for this distribution function. For most compounds, the ideal screening charge density falls within the range of -0.03 to 0.03 e/Å^2. This interval is partitioned in 60 parts, and the histogram (weighted by the area of each segment) of the averaged charge density is computed at each 0.001 e/Å^2 increment. This gives the σ profile for the pure compound. The sigma profile for the combination of cation and anions of the ILs:([BPYRO][PF$_6$], [BPY][PF$_6$], [BPYRO][BF$_4$], [BPY][BF$_4$], and [BeMIM][BF$_4$]) along with TS and PY will be considered here. The sigma profile for the different combination of cation and anions of the ILs,TS, and PY are given in Figures 7a–c.

Figure 7a shows the sigma profiles for three different cations i.e., [BMPYRO], [BMPY] and [BeMIM] and two solute compounds i.e., TS and PY, The two vertical dashed lines in Figures 7a–c are the locations of the cut-off values for the hydrogen bond donor ($\sigma_{\text{hb}} < -0.0082$ e/A^2) and acceptor($\sigma_{\text{hb}} > 0.0082$ e/A^2). The importance of this cut-off value lies in the fact that profile lying in the left side of $\sigma_{\text{hb}} = -0.0082$ e/A^2 will have high donator ability and right side of $\sigma_{\text{hb}} = +0.0082$ e/A^2 will have high acceptor ability. Profiles lying in the negative region are due to inherent positive charge of the atom/molecule and vice versa for the positive region of profile. The sigma profile for [BMPYRO], [BMPY], and [BeMIM], are of the similar nature while the prominent peaks of TS and PY molecules lie on the positive side of the sigma profile, which is due to the negative charge on sulfur and nitrogen. Overlapping of the sigma profiles of TS and PY indicates high immiscibility, which proves they do not like each other. The negative screening charges of the all three cations are due to the positive charge residing inside the aromatic ring of the cations. The three cations show peak at the outer most position in the negative direction. It can be seen that for the cations and TS/PY a very small fraction of the profile lies in the donating or acceptor region. Thus weak hydrogen bond is favored between the acidic hydrogen of [BMPYRO], [BMPY], and [BeMIM] cation with TS/PY. It should also be noted that the aromatic ring on the cation offers the H-bond interaction potential with TS and PY owing to its negative charge. The strength of the cations with TS/PY will depend on the hydrogen bond donor or acceptor availability. The cations have a better donating ability since part of the profile lies to the left of cut-off zone i.e., $\sigma_{\text{hb}} < -0.0082$ e/A^2 while the acceptor side is almost nonexistent i.e., right of cut-off zone i.e., $\sigma_{\text{hb}} > +0.0082$ e/A^2. This is expected as cations carry '+ ve' charge. On looking at the sigma profiles it is clear that the sigma profiles of cations and TS/PY are complimentary, thus they like each other, which confirms the presence of CH—π bonding.

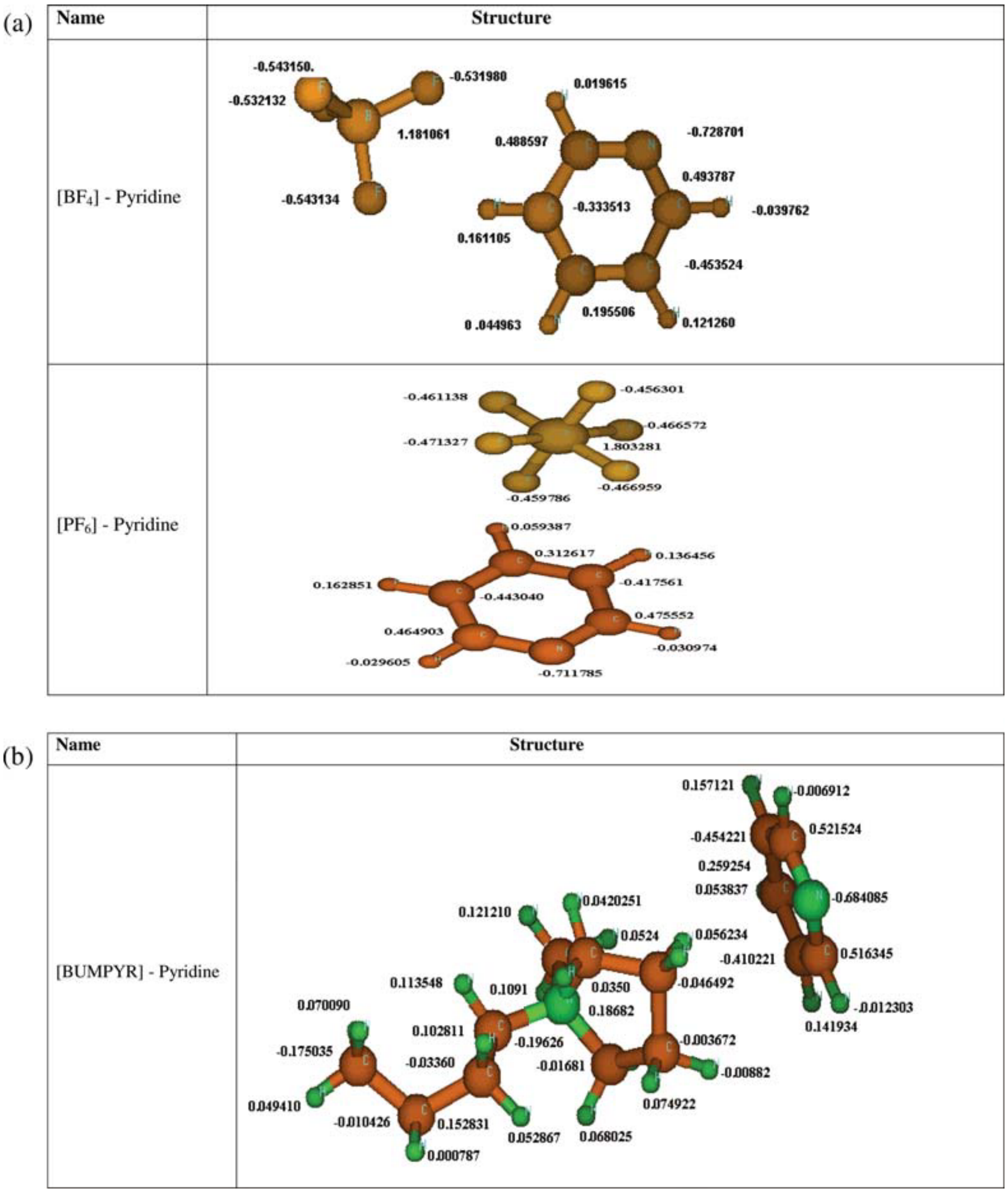

Figure 5. Optimized geometries of cations and anions with pyridine.

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The sigma profiles of anions along with TS and PY are shown in Figure 7b. For the anions i.e., [BF_4] and [PF_6], peaks lie on the right of the cutoff zone for hydrogen bonding, which is due to the inherent negative charges of the anions. However, TS and PY shows peaks at the outmost position in the negative direction. These negative positions of the screening charges are due to the positive charge residing outside the TS and PY molecules. The profiles being complimentary, again confirm the attraction of anions with the aromatic compounds. The sigma profile of five ILs i.e., [BPYRO][PF_6], [BPY][PF_6], [BPYRO][BF_4], [BPY][BF_4], and [BeMIM][BF_4] along with TS and PY molecules have been shown in Figure 7c. The profiles of the cation and anion have been added to get the profile for an Ionic Liquid.[40] The profiles being complimentary show the same information as that of cations and anions explicitly. In other words very few polar surface segments of TS and PY molecules can make energetically acceptable pairs with nonpolar cation on the ionic liquid surface. Thus, it can be concluded that CH–π interaction dominate over the hydrogen bonding effect of sulfur/nitrogen atom with cation.

Conclusions

The ab initio calculations of five ILs, [BPYRO][PF_6], [BPY][PF_6], [BPYRO][BF_4], [BPY][BF_4], and [BeMIM][BF_4] with TS and PY were studied. The effect of various cations: pyridinium, pyrrolidinium, and benzylimidazolium have been studied in detail. The partial charges of nitrogen in PY and sulfur in TS for the simultaneous complex confirmed significant delocalization for the compounds in

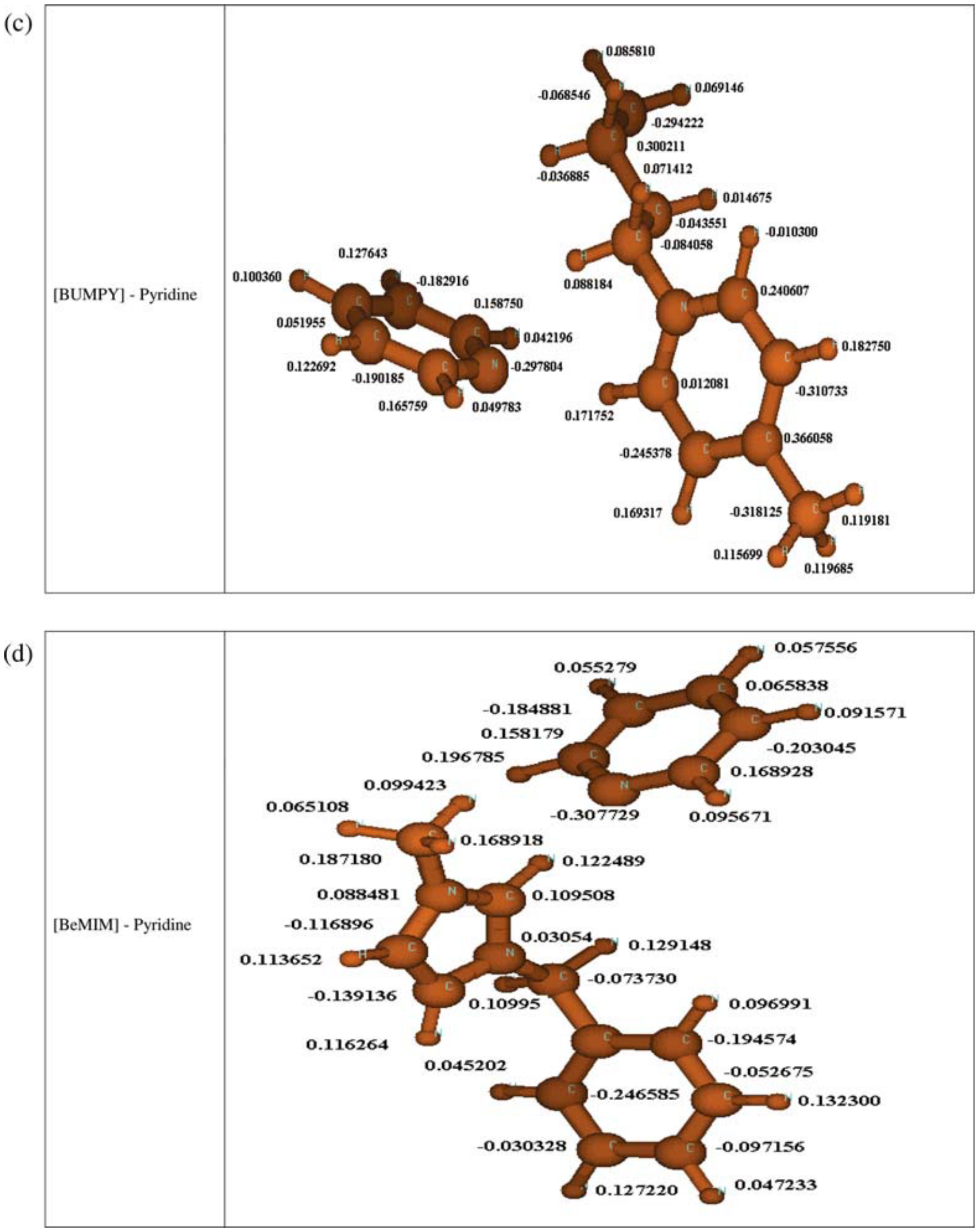

Figure 5. (Continued)

Table 3. Interaction Energy and at Infinite Dilution Activity coefficient (IDAC) for Ionic Liquid Complexes

S. No.	Interaction For The Complex System	[BPYRO][BF$_4$] (kJ/mol)	[BPYRO][PF$_6$] (kJ/mol)	[BPY][BF$_4$] (kJ/mol)	[BPY][PF$_6$] (kJ/mol)	[BeMIM][BF$_4$] (kJ/mol)
1	Thiophene	−4.37	2.275	−10.53	−3.43	−20.48
2	Pyridine	−27.17	3.975	−15.40	−79.06	−27.26
3	Thiophene + Pyridine	−23.39	−33.95	−48.50	−27.37	−30.29
Activity Coefficient at Infinite Dilution via COSMO-RS Model						
1	Thiophene*	2.8272	6.6307	1.7964	3.0726	1.3013
2	Pyridine[†]	0.359	1.6136	1.4571	0.0561	1.1829

*Indicates the COSMO-RS predicted IDAC values of thiophene in ionic liquid.

[†]Indicates the COSMO-RS predicted IDAC values of pyridine in ionic liquid.

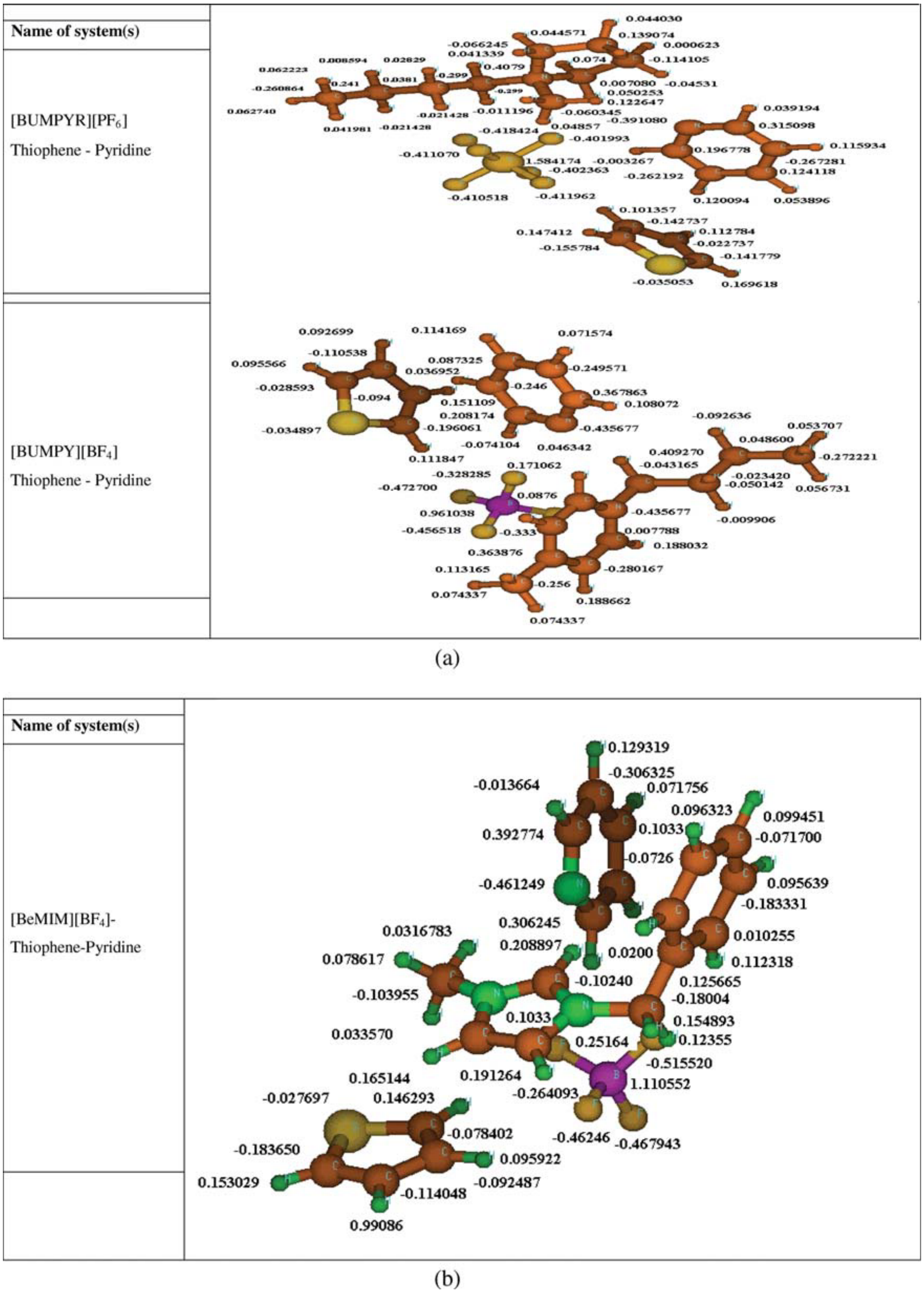

Figure 6. Optimized geometries for IL–thiophene–pyridine.

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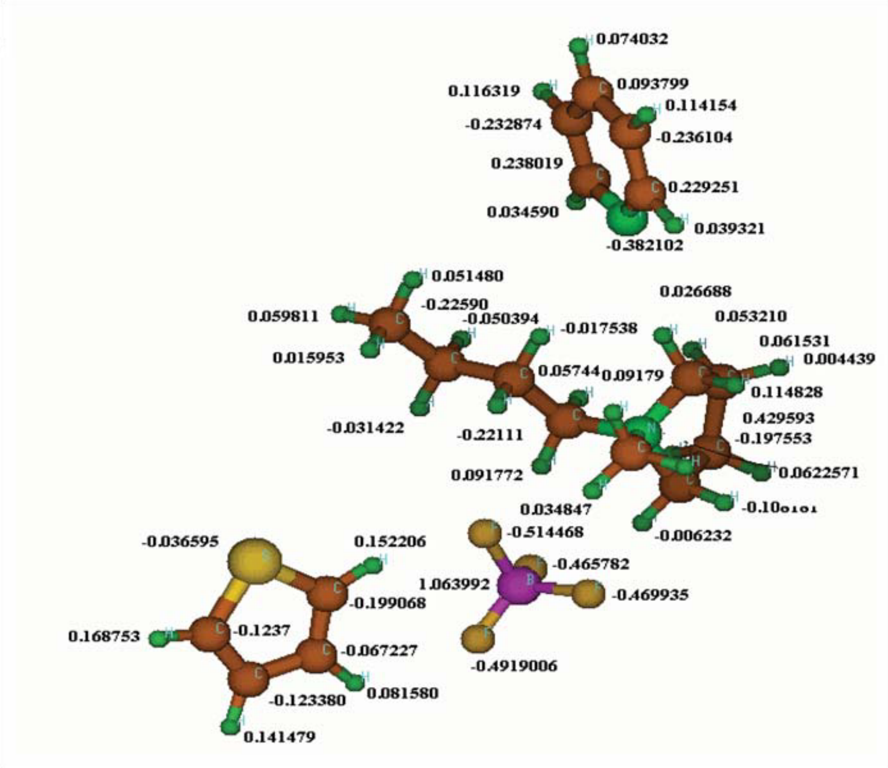
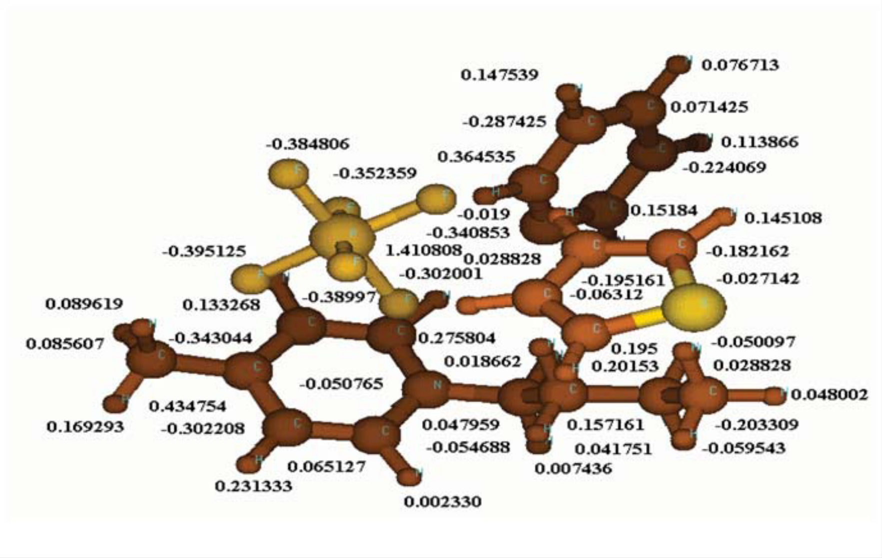
the presence of ILs. For the interaction of IL-TS, the interaction energies followed the order: [BeMIM][BF_4] > [BPYRO][BF_4] >[BPY][BF_4] > [BPY][PF_6] > [BPYRO][PF_6] while for IL-PY, it followed the order: [BPY][PF_6] > [BeMIM][BF_4] > [BPYRO][BF_4] > [BPY][BF_4] > [BPYRO] [PF_6]. A quantitative attempt based on the CH–π interaction in

Name of system(s)	
[BUMPYR][BF$_4$]-Thiophene -Pyridine	

(c)

Name of system(s)	
[BUMPY][PF$_6$]-Thiophene -Pyridine	

(d)

Figure 6. (Continued)

IL-TS-PY complexes gave the interaction energies of ILs in the order: [BPY][BF$_4$] > [BPYRO][PF$_6$] > [BeMIM][BF$_4$] > [BPY][PF$_6$] > [BPYRO][BF$_4$]. Comparing the interaction of cations and TS/PY based on the COSMO-RS approach, a very small fraction of the either profile lay in the donating or acceptor region. Thus, it was concluded that CH–π interaction were found to be dominant when compared with hydrogen bonding effect of sulfur/nitrogen atom with cation.

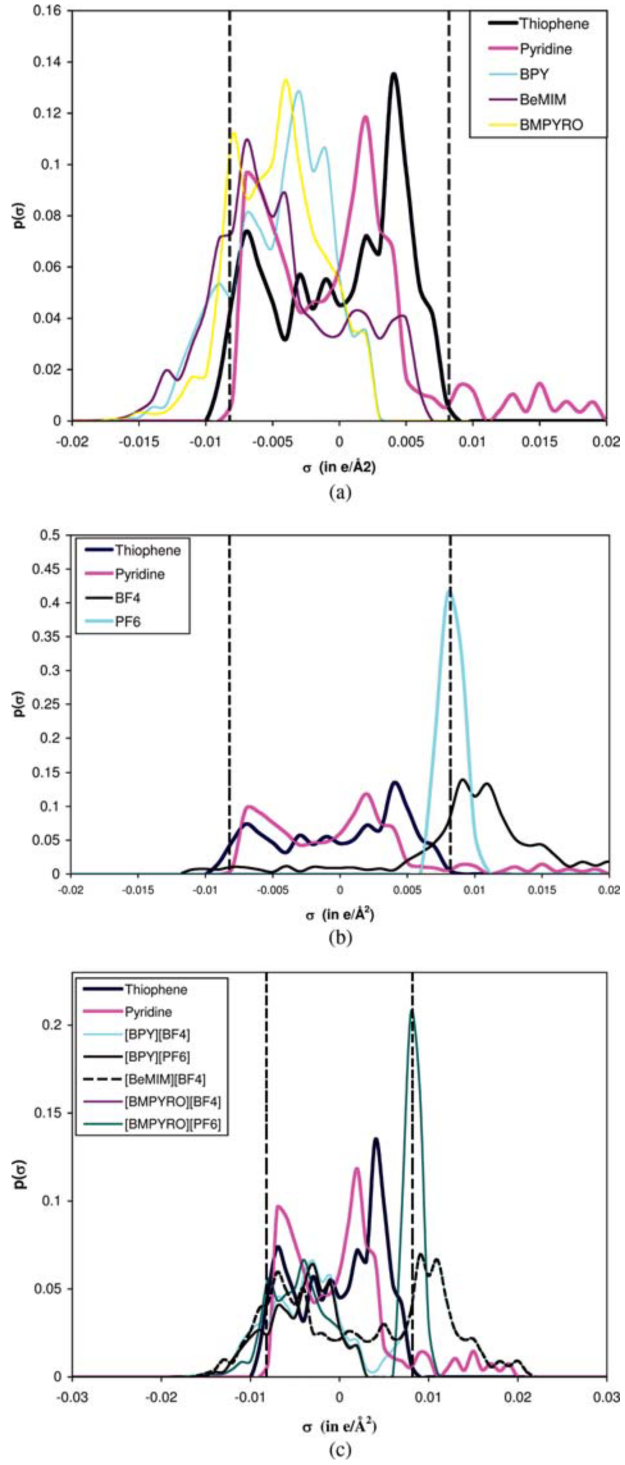


Figure 7. (a) Sigma profiles for cations, thiophene, and pyridine. (b) Sigma profiles for anions, thiophene, and pyridine. (c) Sigma profiles for ILs, thiophene, and pyridine.

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Notation

List of symbols

[BeMIM] = 1-benzyl-3-methylimidazolium
[BUMPYR] = 1-butyl-1-methylpyrrolidinium
[BUMPY] = 1-butyl-4-methylpyridinium
[BF_4] = tetrafluoroborate
[PF_6] = hexafluorophosphate
[BeMIM] [BF_4] = 1-benzyl-3-methylimidazolium tetrafluoroborate
[BUMPYR] [BF_4] = 1-butyl-1-methylpyrrolidinium tetrafuloroborate
[BUMPYR] [PF_6] = 1-butyl-1-methylpyrrolidinium hexafluorophosphate
[BUMPY] [BF_4] = 1-butyl-4-methylpyridinium tetrafluoroborate
[BUMPYR] [PF_6] = 1-butyl-4-methylpyridinium hexafluorophosphate

Greek letters

σ = screening charge density in e/ Å^2
σ_{hb} = cut-off screening charge density for hydrogen bonding in e/Å^2

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