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A quantum chemical study on the molecular interaction between pyrrole and ionic liquids

Hanee Farzana Hizaddin, Ramalingam Anantharaj *, Mohd. Ali Hashim

University of Malaya Centre for Ionic Liquids (UMCiL), Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

Requirement to produce Ultra Low Sulphur Diesel is becoming more stringent with the target of zero emission. The presence of nitrogen compound in crude oil is undesirable because it inhibits the efficiency of desulphurisation process besides being environmentally hazardous when found in transportation fuels. Extractive denitrification with ionic liquids (ILs) as solvents has been found to be applicable for denitrification but more insights are required to explain the interaction between ILs and nitrogen compounds. In this study, the interaction between pyrrole as model nitrogen compound with 18 ILs built from 6 cations and 3 anions is investigated by means of quantum chemical calculation. Geometry optimisation was done for individual molecules of pyrrole, cations and anions, as well as complexes of ILs, pyrrole–cation, pyrrole–anion, pyrrole–IL at Hartree–Fock level and 6-31G* basis set. NBO analysis was performed from the optimised geometry for each molecule and complex. The interaction between pyrrole and ILs is investigated via HOMO and LUMO energy values and gaps, global scalar properties, interaction energies and partial charges. It was found that [EPY][EtSO$_4$] is the most favourable IL for the removal of pyrrole.

1. Introduction

With the growing concern towards reducing emission from transportation fuels to the environment, the requirement to produce low-sulphur fuels is becoming more stringent. The current limit for sulphur content in diesel fuel is less than 10 ppm for the production of Ultra Low-Sulphur Diesel (ULSD) with the target of zero emission in the future. However, the presence of nitrogen compounds even at low concentration hinders the efficiency of sulphur removal from diesel fuels. Laredo et al. [1,2] reported that the presence of nitrogen compounds as low as <30 ppm inhibits the efficiency of hydrodesulphurisation process through competitive adsorption, making it more difficult to meet the low-sulphur requirement. Besides the inhibition effect, the presence of nitrogen compounds in diesel is also non-desirable, because it can cause coke formation and lead to catalyst deactivation. Also, the presence of nitrogen compounds may possibly affect the stability of diesel during storage. Therefore, in order to achieve high sulphur removal, knowledge on the removal of nitrogen compounds is essential [3].

The common practice in industry for removal of nitrogen is hydrodenitrification (HDN) and for removal of sulphur is hydrodesulphurisation (HDS). These processes are energy intensive and are costly due to the high operating temperature (300–400 °C) and elevated pressure (20–100 atm of H$_2$). This drives the research community to search for alternative processes for the removal of sulphur and nitrogen compounds. Solvent extraction process such as extractive desulphurisation and extractive denitrification is seen as a potentially promising candidate to replace HDS and HDN, since it is a much simpler process, it can be operated at ambient temperature and pressure without much modification on the equipment, thus lowering the operating cost and energy consumption. The efficiency of extraction process however depends upon the performance of the solvent. Solvent selection is therefore crucial in order to achieve high nitrogen removal from liquid fuels.

Ionic liquids have emerged as a potentially versatile solvent for various applications including for liquid extraction process. Properties of ionic liquids include high thermal stability, high electrochemical stability, wide liquid range, and high ionic conductivity [4]. Ionic liquid is also known as “designer solvent” as it can be designed to suit a preferred separation process by predetermining its composition through altering the anion–cation combination and its substituents. The tunability of ionic liquids is also the main reason why it is explored for various applications. In recent years, several authors have reported the use of ionic liquids as solvents to remove nitrogen compounds from gasoline and diesel. Kedra-Krolik et al. [5,6], Zhang et al. [7] and Alonso et al. [8] reported the use of imidazolium-based ionic liquids with various anions to remove aromatic sulphur and nitrogen compounds from model diesel oils and concluded that these ILs demonstrated good capacity for desulphurisation as well as denitrification. Chloride-based ILs [9,10] and dicyanamide-based ILs [11,12] have also been used for selective extraction of nitrogen compounds; with

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* Corresponding author. Tel.: +60 3 7967 7687.
E-mail address: anantharaj@um.edu.my (R. Anantharaj).

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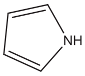
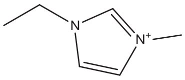
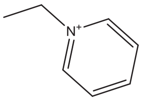
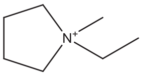
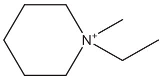
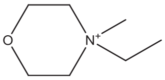
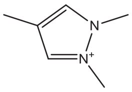
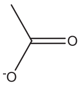
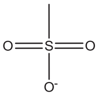
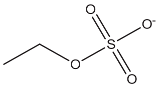
competitive selectivity and capacity towards nitrogen compounds. Thus, it is evident that ionic liquids have great potential to be further utilised as solvent for denitrification of liquid fuels.

However, although the number of publications reporting on the use of various ionic liquids for denitrification purposes is increasing, it is still considered low when compared to the infinite number of possible ionic liquids which could be synthesised. Furthermore, these works only report the suitable ILs for the purpose of denitrification process based on phase equilibria data, selectivity and capacity of the systems with ILs without giving much insights on the interactions between the species involved. In order to design an IL for denitrification, a systematic approach must be taken and knowledge on the reactivity and stability of interacting system is essential. Ab initio method such as quantum chemical calculation provides an alternative to achieve this objective with the advantage of not requiring a huge base of experimental data. Instead, only the structure of the species involved is required as an input to the calculation.

In recent times, the number of literature related to ab initio calculations describing the interactions between organic solute and ionic liquids for separation processes including desulphurisation and denitrification has increased. Zhang et al. [13] investigated the interactions between thiophene and the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) by performing geometry optimisation on five clusters of thiophene–cation, thiophene–anions and thiophene–ILs. It was discovered that the interaction of thiophene with ILs is mainly via Coulombian attraction and that stronger electron donation to the fluorine atoms and compactness of the ILs influences the interaction with thiophene. Anantharaj et al. reported HOMO/LUMO energy values and gap with global scalar properties to investigate simultaneous interaction for the systems of IL with thiophene and pyridine [14], where geometry optimisation calculations were done for the molecules thiophene, pyridine, the cations 1-butyl-3-methylpyrrolidinium ([BMPYRO]), 1-butyl-3-methylpyridinium ([BMPY]) and benzylimidazolium ([BeMIM]), and the anions tetrafluoroborate ([BF_4]) and hexafluorophosphate ([PF_6]), as well as the complexes of thiophene–pyridine–IL, thiophene–IL and pyridine–IL. The same group later performed quantum chemical studies consisting of determination of partial charges, interaction energies and sigma profile generation (based on COSMO-RS theory) to study simultaneous interactions thiophene and pyridine with the ILs [BMPYRO][BF_4], [BMPYRO][PF_6], [BMPY][BF_4], [BMPY][PF_6] and [BeMIM][BF_4] [15]. The result based on each approach agrees well with each other and confirms the description of the interactions in each system which demonstrates the dominance of CH–π interaction. More recently, geometry optimisation based on DFT calculations for the interactions between the ILs [BMIM][PF_6] and [BMIM][BF_4] with pyridine/hexane was performed and it was concluded that the interactions between the studied ILs with pyridine are stronger than that of between ILs and hexane [16].

In this work, the interactions of a 5-membered non-basic nitrogen compound, pyrrole, with 18 ionic liquids built from the combination of 6 cations and 3 anions are investigated based on quantum chemical calculations by determining the HOMO/LUMO energy values and energy gap, scalar properties, interaction energies and atomic charges of the species and its complexes. The structure of pyrrole, cations and anions is presented in Table 1.

Table 1
Structure of the species involved in this work.

Compound	Name	Structure	Abbreviation	Chemical formula	MW
Nitrogen compound	Pyrrole		PYR	C_4H_5N	67
Cations	1-Ethyl-3-methylimidazolium		[EMIM]	$C_6H_{11}N_2$	111
	1-Ethylpyridinium		[EPY]	$C_7H_{10}N$	108
	1-Ethyl-1-methylpyrrolidinium		[EMPYRO]	$C_7H_{16}N$	114
	1-Ethyl-1-methylpiperidinium		[EMPIPE]	$C_8H_{18}N$	128
	4-Ethyl-4-methylmorpholinium		[EMMOR]	$C_7H_{16}O$	116
	1,2,4-Trimethylpyrazolium		[TMPYRA]	$C_6H_{11}N_2$	111
Anions	Acetate		[Ac]	CH_3COO	59
	Methylsulphonate		[$MeSO_3$]	CH_3SO_3	95
	Ethyl sulphate		[$EtSO_4$]	$C_2H_5SO_4$	125

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