THEORETICAL STUDY ON INTERACTIONS BETWEEN CU-BASED IONIC LIQUID AND PROPANE/PROPYLENE

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ABSTRACT

Density functional theory has been employed to investigate the interactions between copper(I) bis(trifluoromethylsulfonyl)imide (Cu[Tf2N]) and C3H6/C6H6. The calculations were based on the model of Cu[Tf2N], and performed at X3LYP/6-31++G** level. The calculated interaction energies indicated that the adsorption ability of Cu[Tf2N] for C3H6/C6H6 followed the order of C3H6 < C6H6. The noncovalent interactions in real space, based on the electron density and its derivatives, reveal the nature of interactions between Cu[Tf2N] and C3H6/C6H6. The natural bond orbital (NBO) analysis of the second-order perturbation energy has been performed to investigate the interaction mechanism of C3H6/C6H6 on ionic liquid Cu[Tf2N].

Key Words: Cu-Based Ionic Liquid, Interaction, C3H6/C6H6

1 INTRODUCTION

The recovery of light olefins from the off-gas of catalytic crackers is an important process in the petrochemical industry. Propylene is the raw material for the polypropylene production, a polymer of extensive applications. The separation of olefin/paraffin gas mixtures by low temperature distillation is one of the most important but also most energy-consuming separation processes. Development of economically viable propylene/propane separation processes is becoming increasingly important, but it is extremely challenging due to the physicochemical similarities between those two molecules. Among a number of alternatives separation processes, reactive absorption of olefins from olefin/paraffin mixtures using a silver salt solution as absorption liquid in a gas/liquid membrane contactor may be attractive in this respect [1-7]. Room temperature ionic liquids are proposed as potential substitutes for conventional solvents as reaction media, such as a negligible volatility, which enables a relatively easy recovery, a wide range of polarities, non-flammable compounds, and high chemical and thermal stability. Besides, their lack of volatility gives ionic liquids the feature that they can perform gas separations without solvent losses or gas stream pollution.

The bis(trifluoromethanesulfonyl)imide (also known as bis(triflyl)imide, NTf2) salts of the coinage metal ions Cu+ and Ag+ have been synthesized [8-10]. It was reported that Ag[Tf2N] ionic liquid can be used to separate propane/propylene or ethylene/ethane [1,3,11,12]. Due to the cheap metal of copper and its similar properties in contrast to silver, Cu[Tf2N] may be potential to be as sorbent for separation of propane/propylene, so the interactions between Cu[Tf2N] and propane/propylene by theoretical methods were compared. The structures of Cu[Tf2N], propane, and propylene are shown in Fig. 1.

![Fig. 1 The structures of (a) Cu[Tf2N], (b) C3H6 and (c) C6H6](image_url)

2 Computational details

The extended hybrid density functional X3LYP [13], which is wildly used in ionic liquids [14,15], reveals excellent performance, hence we used this method which is good at describing the van der Waals and hydrogen bonding interactions [16]. The 6-31++G(d,p) basis set (5d, 7f spherical-harmonic type) has been employed in all the calculations since they can give a fine compromise between accuracy and computational cost. No symmetry constraint was imposed on the optimization of initial structures. To examine the nature of interactions, the electronic properties for stationary points were illustrated in terms of natural bond orbital (NBO) analysis [17]. The NBO analysis was obtained with 6-31++G** basis set to provide information of hydrogen bonding and halogen bonding. Multiwfns softpackage [18,19] was employed to analyze the interaction properties.

For interaction energy, basis set superposition errors (BSSE) were considered using the counterpoise method [20] and the relative energy of certain structure is defined as the difference relative to the most stable structure, which was calculated as following:

\[ E = E([Cu[Tf2N]-C3H6/C6H6]) - (E([Cu[Tf2N]]) + E(C3H6/C6H6)) \]

3 RESULTS AND DISCUSSION

3.1 Geometric, electronic properties and interaction energies

In this section, we discuss the most stable geometries of Cu[Tf2N]-C3H6 and Cu[Tf2N]-C6H6. Fig. 2 shows the two most stable geometries optimized at the X3LYP 6-31++G(d,p) level, frequency analyses of all stationary points have been performed with the same level calculations to guarantee the most stable geometries of the molecules. Some important structural parameters, including the distances and NBO charge between Cu[Tf2N] and C3H6/C6H6 are listed. The distances of Cu⋯H11, Cu⋯H12 and Cu⋯C1 in Cu[Tf2N]-C3H6 are 1.833 Å, 1.836 Å and 2.157 Å, less than the sum of van der Waals radii of Cu (1.4 Å), H (1.20 Å), and C (1.70 Å) [21]. While the Cu⋯C1 and Cu⋯C2 distances in Cu[Tf2N]-C6H6 are 2.004 Å, 2.053 Å, respectively, which suggest the strong interactions between Cu[Tf2N] and C6H6.

The interaction energies between Cu[Tf2N] and C3H6/C6H6 were 18.63 Kcal/mol and 40.16 Kcal/mol, respectively, demonstrating that the interaction between Cu[Tf2N] and C3H6 is weaker than that between Cu[Tf2N] and C6H6.
3.2 NBO analysis

The optimized structures were employed for NBO analysis. NBO analysis is based on a method for optimally transforming a given wave function into localized form, corresponding to the one-center (lone pairs) and two-center (bonds) elements of the chemist’s Lewis structure picture. It provides a better description of the electron distribution in complexes. The NBO analysis were performed for Cu[Tf2N]-C-H and Cu[Tf2N]-C-H. The NBO charges (Fig. 2) of N and Cu in Cu[Tf2N]-C-H and Cu[Tf2N]-C-H are -1.35701, 0.78874, and -1.34923, 0.89375, respectively, suggesting that the more negative charges of H11 and H12 migrate to Cu in Cu[Tf2N]-C-H, and the more positive Cu in Cu[Tf2N]-C-H may be ascribed to its back-donation.

Table 1 gives the natural electron configurations of Cu, N, S2, S1, H11, H12 or C1, C2 of Cu[Tf2N]-C-H and Cu[Tf2N]-C-H. The electron configurations of copper in Cu[Tf2N]-C-H and Cu[Tf2N]-C-H are [core] 3d^10s^0p^5^0^0 and [core] 3d^10s^0p^5^0^0, respectively, indicating the more decreasing of 3d orbital electrons of Cu[Tf2N]-C-H in contrast to that of Cu[Tf2N]-C-H. The C1 and C2 electron configurations in Cu[Tf2N]-C-H are [core] 2s^12p^10^4s^0^4p^5^0 and [core] 2s^12p^10^4s^0^4p^5^0, respectively, demonstrating the net electron migration from copper to C1 and C2.

The linear combination of natural atomic orbitals (NAOs) of Cu[Tf2N]-
C-H and Cu[Tf2N]-C-H are tabulated in Table 2. It can be seen the fact that the occupancy for LP(5)Cu (3d) and LP*(6)Cu (4s) in Cu[Tf2N]-C-H and Cu[Tf2N]-C-H are 1.9715, 0.25213 and 1.81391, 0.29997, respectively, demonstrating the main charge transfer between Cu[Tf2N] and π(C1-C2), π*(C1-H11). The occupancy of σ*(C1-H13), σ*(C1-H12), and σ*(C1-H11) indicates the charge transfer to anti-orbital of C1-H2, while the occupancy of σ(C1-C2), π(C1-C2), σ*(C1-C2) and π*(C1-C2) is 1.99157, 0.11616 and 0.23584, demonstrating the main charge transfer between Cu[Tf2N] and π(C1-C2), π*(C1-C2) orbitals of C1-H2.

Table 1 The natural electron configurations of Cu, N, S2, S1, H11, H12 or C1, C2 of Cu[Tf2N]-C-H and Cu[Tf2N]-C-H.

|            | Cu[Tf2N]-C-H   | Cu[Tf2N]-C-H   |
|------------|----------------|----------------|
| Cu         | [core] 3d^10s^0p^5^0^0 | [core] 3d^10s^0p^5^0^0 |
| N          | [core] 2s^12p^10^4s^0^4p^5^0 | [core] 2s^12p^10^4s^0^4p^5^0 |
| S2         | [core] 3s^1^3p^3^3d^10^4p^5^0 | [core] 3s^1^3p^3^3d^10^4p^5^0 |
| S1         | [core] 3s^1^3p^3^3d^10^4p^5^0 | [core] 3s^1^3p^3^3d^10^4p^5^0 |
| H11        | 1s^0 | C1 | [core] 2s^1^3p^3^3d^10^4p^5^0 |
| H12        | 1s^0 | C2 | [core] 2s^1^3p^3^3d^10^4p^5^0 |

Table 2 The linear combination of natural atomic orbitals (NAOs) of Cu[Tf2N]-C-H and Cu[Tf2N]-C-H.

|          | Cu[Tf2N]-C-H   | Cu[Tf2N]-C-H   |
|----------|----------------|----------------|
| NBO      | occupancy     | NAO            | occupancy     | NAO            |
| LP(1)Cu  | 1.99900        | 3d             | LP(1)Cu      | 1.99769        | 3d             |
| LP(2)Cu  | 1.99746        | 3d             | LP(2)Cu      | 1.99656        | 3d             |
| LP(3)Cu  | 1.98856        | 3d             | LP(3)Cu      | 1.99076        | 3d             |
| LP(4)Cu  | 1.97873        | 3d             | LP(4)Cu      | 1.98905        | 3d             |
| LP(5)Cu  | 1.97755        | 3d             | LP(5)Cu      | 1.81391        | 3d             |
| LP*(6)Cu | 0.25213        | 4s             | LP*(6)Cu     | 0.29997        | 4s             |
| σ*(C1-H13)| 0.00948    | 0.5595(sp^1^10^0) | σ*(C1-C2) | 1.99157 | 0.7034(sp^1^10^0) |
| σ*(C1-H12)| 0.02281    | 0.6230(sp^1^10^0) | π(C1-C2)  | 1.83797 | 0.7340(sp^1^10^0) |
| σ*(C1-H11)| 0.02259    | 0.6249(sp^1^10^0) | σ*(C1-C2) | 0.01166 | 0.7108(sp^1^10^0) |
| π*(C1-C2) | 0.23584     | 0.6792(sp^1^10^0) | π*(C1-C2) | 0.23584 | 0.6792(sp^1^10^0) |
Some donor-acceptor interactions in Cu[Tf$_N$]-C$_4$H$_8$. Cu[Tf$_N$]-C$_4$H$_8$ and their second order perturbation stabilization energies, $E(2)$ (kcal/mol)

| Donor      | Acceptor     | $E(2)$ (kcal/mol) | Donor      | Acceptor     | $E(2)$ (kcal/mol) |
|------------|--------------|------------------|------------|--------------|------------------|
| LP(2)Cu    | $\sigma^*(C1-H12)$ | 0.19             | LP(2)Cu    | $\sigma^*(C1-H11)$ | 0.16             |
| LP(4)Cu    | $\sigma^*(C1-H11)$ | 3.39             | LP(3)Cu    | $\sigma^*(C1-H13)$ | 0.61             |
| LP(5)Cu    | $\sigma^*(C1-H12)$ | 3.04             | LP(4)Cu    | $\sigma^*(C1-H12)$ | 0.74             |
| LP*(6)Cu   | $\sigma^*(C3-H33)$ | 0.17             | LP(5)Cu    | $\sigma^*(C1-H11)$ | 0.42             |
| LP*(6)Cu   | $\sigma^*(C2-C1)$ | 0.46             | LP*(6)Cu   | $\sigma^*(C3-H32)$ | 0.05             |
| LP*(6)Cu   | $\sigma^*(C1-H11)$ | 0.65             | LP*(6)Cu   | $\sigma^*(C1-H13)$ | 0.80             |
| LP*(3)Cu   | $\sigma^*(C3-H32)$ | 0.35             | LP*(6)Cu   | $\sigma^*(C1-H12)$ | 0.59             |
| LP(3)Cu    | $\sigma^*(C3-C2)$ | 0.18             | LP*(6)Cu   | $\sigma^*(C3-H32)$ | 0.41             |
| LP(5)Cu    | $\sigma^*(C1-H12)$ | 0.18             | LP*(6)Cu   | $\sigma^*(C2-H21)$ | 0.17             |
| LP*(6)Cu   | $\sigma^*(C1-H12)$ | 0.17             | LP*(6)Cu   | $\sigma^*(C1-H11)$ | 0.19             |

Some donor-acceptor interactions in Cu[Tf$_N$]-C$_4$H$_8$. Cu[Tf$_N$]-C$_4$H$_8$ and their second order perturbation stabilization energies are given in Table 3. The main interactions in Cu[Tf$_N$]-C$_4$H$_8$ are LP(4)Cu→$\sigma^*(C1-H11)$, LP(5)Cu→$\sigma^*(C1-H12)$, LP(3)Cu→LP*(6)Cu, and LP(1)Cu→LP*(6)Cu, exhibiting the strong interactions between $\sigma(C1-H12)$, $\sigma(C1-H11)$ and 4s$^*$ orbital. While the main interactions in Cu[Tf$_N$]-C$_4$H$_8$ are LP(5)Cu→$\sigma^*(C1-C2)$, $\sigma(C1-C2)$→LP*(6)Cu, $\sigma(C1-H11)$→LP*(6)Cu, $\sigma(C1-H12)$→LP*(6)Cu, $\sigma(C2-C3)$→LP*(6)Cu, $\sigma(C2-H21)$→LP*(6)Cu, $\sigma(C1-H12)$→LP*(6)Cu, demonstrating the strong interactions due to charge transfer from $\pi(C1-C2)$ to 4s$^*$ and back donation from d orbital to $\pi^*(C1-C2)$. The significant differences between Cu[Tf$_N$] and C$_4$H$_8$/C$_4$H$_8$ are that $\pi(C1-C2)$ and $\pi^*(C1-C2)$ are involved in the interactions.

3 Visualization of weak interactions with real space functions

Yang and co-workers recently presented a new method for studying non-covalent interactions in and between molecules [22]. The non-covalent interaction analysis is based on considering three components of the electron density distribution: the density itself ($\rho$), the reduced gradient of the density ($\nabla^2 \rho(r)$), and the Laplacian of the density ($\nabla^2 \rho$). The Laplacian is further decomposed into three eigenvalues ($\lambda_1 \leq \lambda_2 \leq \lambda_3$). The second component, $\nabla^2 \rho$, contains the interesting information; when $\lambda_3 < 0$, the interaction is bonding, while $\lambda_3 > 0$, the interaction is nonbonding [23]. According to the above three properties of the electron density, three main types of non-covalent interactions: attractive, moderately strong (e.g., hydrogen bonds), repulsive, moderately strong (e.g., steric interactions), and weak dispersion type interactions were identified. The Sign($\lambda_3$), $\rho$-RDG(r), and the color-filled graph of weak interaction regions($\text{Sign}(\lambda_3)$-$\rho$-RDG(r) isosurface) of Cu[Tf$_N$]-C$_4$H$_8$, and Cu[Tf$_N$]-C$_4$H$_8$ were depicted in Fig. 3 and Fig. 4.

The weak interactions always exist in the place of small $\rho(r)$ and 0 ~ medium RDG(r). The scatter diagrams of $\rho(r)$-RDG(r) are helpful for notarizing the existence of weak interactions. The subsistent splattering area of small $\rho(r)$ and 0 ~ medium RDG(r) was addressed as “spike”, and it accounts for the existence of weak interactions in the complex [22]. It can be found that plots of the electron density ($\rho$) and its reduced density gradient for Cu[Tf$_N$]-C$_4$H$_8$ and Cu[Tf$_N$]-C$_4$H$_8$ have “spikes”, suggesting the occurrence of weak interactions. In order to classify the types of weak interactions, the scatter diagrams of $\text{Sign}(\lambda_3)$-$\rho$-RDG(r) for Cu[Tf$_N$]-C$_4$H$_8$ and Cu[Tf$_N$]-C$_4$H$_8$ were depicted. Large, negative values of $\text{Sign}(\lambda_3)$ are indicative of hydrogen bonding interactions; while large, positive values of $\text{Sign}(\lambda_3)$ are indicative of hydrogen bonding interactions with van der Waals interactions, and large, positive $\text{Sign}(\lambda_3)$ are indicative of hydrogen bonding interactions with van der Waals interactions.

Dapprich, and Frenking [24] put forward a partitioning scheme for analyzing donor-acceptor interactions in a complex. The charge decomposition analysis constructs the wave function of the complex in terms of the linear combination of the donor and acceptor fragment orbitals (LCO). Three terms, the charge donation $d$, the back donation $b$, and the charge depletion from the overlapping area (charge polarization) $r$ were calculated for each LCO orbital of the complex. The sum of the three contributions gives the total amount of donation, back donation and charge polarization in the complex. The number of electrons donated from Cu[Tf$_N$] to C$_4$H$_8$/C$_4$H$_8$ ($d$), the number of electrons back donated from C$_4$H$_8$/C$_4$H$_8$ to Cu[Tf$_N$] ($b$), and the number of electrons involved in repulsive polarization ($r$) are listed in Table 4. It can be seen that the weak electron donation Cu[Tf$_N$]-C$_4$H$_8$ (0.0054 e) and strong back donation C$_4$H$_8$/Cu[Tf$_N$] (0.1341 e) occur, while the net charge transfer from Cu[Tf$_N$] to C$_4$H$_8$ is 0.761. The calculated charge polarization is quite different, It is -0.117 e for Cu[Tf$_N$]-C$_4$H$_8$ and -0.082 e for Cu[Tf$_N$]-C$_4$H$_8$, respectively.
The density difference can be employed to locate ranges of charge depletion and charge concentration. A related scheme uses the calculation of the Laplacian $\nabla^2 \rho(r)$ of the density distribution $\rho(r)$, which determines the regions in space wherein electronic charge is locally concentrated and depleted. The electron density differences of $\text{Cu[Tf}_2\text{N]}\rightarrow\text{C}_3\text{H}_6$ and $\text{Cu[Tf}_2\text{N]}\rightarrow\text{C}_3\text{H}_8$ shown in Fig. 5 reflect the redistribution of electron. It can be found that the electronic charge between two hydrogen atoms is depleted and electronic charge of the $\sigma^*$ orbital in $\text{C}_3\text{H}_6$ is concentrated in $\text{Cu[Tf}_2\text{N]}\rightarrow\text{C}_3\text{H}_8$. The depletion of electronic charge of $\pi$ orbital in $\text{C}_3\text{H}_8$ and $d$ orbital of $\text{Cu}$, the concentration of electronic charge of $\pi^*$ orbital in $\text{C}_3\text{H}_6$ demonstrate the charge transfer from $\pi$ orbital in $\text{C}_3\text{H}_8$ to $4s^*$ orbital of $\text{Cu}$, and back donation from $d$ orbital of $\text{Cu}$ to $\pi^*$ orbital in $\text{C}_3\text{H}_6$, in agreement with the NBO analysis.

The number of electrons donated from $\text{Cu[Tf}_2\text{N]}\rightarrow\text{C}_3\text{H}_6$ (d), the number of electrons back donated from $\text{C}_3\text{H}_6\rightarrow\text{Cu[Tf}_2\text{N]}$ (b), and the number of electrons involved in repulsive polarization (r)

|      | Cu[Tf,N]-C₃H₈  | Cu[Tf,N]-C₃H₁₀ | d-b     | r       |
|------|----------------|----------------|---------|---------|
| Cu[Tf,N]-C₃H₈  | 0.005403       | 0.134097       | -0.128694 | -0.117491 |
| Cu[Tf,N]-C₃H₁₀ | -0.048576      | -0.809535      | 0.760959  | -0.082345 |
CONCLUSIONS

The molecular structures and nature of interactions between copper(I) bis(trifluoromethylsulfonylimide) and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6} were investigated on the basis of ab initio method. The most stable structures of Cu[Tf\textsubscript{2}N]-C\textsubscript{3}H\textsubscript{8} and Cu[Tf\textsubscript{2}N]-C\textsubscript{3}H\textsubscript{6} indicate the significant differences between Cu[Tf\textsubscript{2}N] and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6}. The nature of interactions between Cu[Tf\textsubscript{2}N] and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6} were investigated by NBO analysis, charge decomposition analysis, and analyses of weak interactions with several real space functions, demonstrating the formation of chemical bonds between Cu[Tf\textsubscript{2}N] and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6}. The remarkably different interaction energies between Cu[Tf\textsubscript{2}N] and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6} imply that Cu[Tf\textsubscript{2}N] ionic liquid may be used to separate C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6} mixture.

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