CHAPTER V
CONCLUSION AND RECOMMENDATIONS

Five room temperature ionic liquids, triethylsulfonium bis(trifluoro methylsulfonyl)imide ($[S_{222}][Tf_2N]$), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethyl sulfonyl)imide ($[deme][Tf_2N]$), 1-propyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ($[pmim][Tf_2N]$), 1-allyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ($[amim][Tf_2N]$), and 1-butyl-4-methylpyridinium tetrafluoroborate ($[4mbp][BF_4]$) are studied measuring their densities and their capacities to absorb CO_2. The densities were measured at atmospheric pressure at temperatures ranging from 278.15 K to 353.15 K. The densities decrease linearly with increase in temperature and diminish in the following order: $[amim][Tf_2N] > [pmim][Tf_2N] > [S_{222}][Tf_2N] > [deme][Tf_2N] > [4mbp][BF_4]$.

Experimental CO_2 solubility measurements in the ionic liquids $[S_{222}][Tf_2N]$, $[deme][Tf_2N]$, $[pmim][Tf_2N]$, $[amim][Tf_2N]$, and $[4mbp][BF_4]$ were carried out at 313.15, 323.15 and 333.15 K at different pressures under 20 bar using a gravimetric microbalance (IGA-003). Temperature and pressure dramatically affect the solubility of CO_2 in these ionic liquids. For all of the ionic liquids studied, the solubility decreases as temperature increases and pressure decreases. Regarding the effect of double bond, the ionic liquid $[amim][Tf_2N]$ having a double bond on the alkyl chain of the cation exhibits higher polarity than $[pmim][Tf_2N]$, therefore lowering the solubility of CO_2. The absorption of CO_2 in the ionic liquids tends to decrease in this sequence: $[deme][Tf_2N] > [pmim][Tf_2N] > [amim][Tf_2N] > [S_{222}][Tf_2N] > [4mbp][BF_4]$. The four ionic liquids ($[deme][Tf_2N]$, $[pmim][Tf_2N]$, $[amim][Tf_2N]$ and $[S_{222}][Tf_2N]$) have been proven as potential alternatives for CO_2 capture due to high CO_2 solubility with physical absorption comparable to other physical ionic liquids with high fluorination, such as $[hmim][Tf_2N]$ and [hmim][eFAP]. The solubilities of CO_2 in the studied ionic liquids are much less than that in [bmim][Ac], which exhibits a strong chemical absorption and the reported formation of a chemical complex. However, more energy is required to regenerate a solvent that reacts chemically when compared to physical solvent.

The ammonium-based ionic liquid [deme][Tf_2N] is apparently the most promising physical solvent for CO_2 capture due to an evidence showing the highest solubility of CO_2 among the ionic liquids studied.

As far as modeling, the normal boiling temperatures, critical temperatures and pressures, and the acentric factors of the ionic liquids were estimated with the modified Lydersen-Joback-Reid method. The standard Peng-Robinson (PR-EoS), the standard Redlich-Kwong-Soave (SRK-EoS) and the SRK-EoS with quadratic mixing rules as well as the Non-Random Two-Liquid (NRTL) activity coefficient model were used to correlate the experimental data for the binary systems of CO_2 + ionic liquids. The modeling results suggest that the SRK with quadratic mixing rules and the NRTL can satisfactorily model the solubility of CO_2 in the studied ionic liquids at low pressure up to 20 bar and temperatures of 313.15, 323.15 and 333.15 K. Henry's law constants and the enthalpies and entropies of absorption for the studied ionic liquid + CO_2 systems were determined. It is concluded that the solubility of CO_2 decreases with rising temperature, thus reducing Henry's law constant. Significant interactions and ordering between the ionic liquids and CO_2 are therefore observed. Absorption of CO_2 is an exothermic process and decreases the order of the ionic liquids due to the negative values of enthalpies and entropies of absorption, respectively.

The investigations on the solubility of CO_2 in these ionic liquids were performed at low pressure due to the limitation of the apparatus being able to be operated under 20 bar, which is applicable to CO_2 capture processes. It is recommended that the knowledge of high pressure solubility of these ionic liquids is necessary for further studies in order to apply for natural gas processing. Although ionic liquids are regarded as green alternatives due to their negligible vapor pressure which minimizes contamination to atmosphere. However, low volatility does not completely eliminate potential environmental hazards. Some ionic liquids might have serious threats to aquatic ecosystems. To the best of our knowledge, the chemical, physical, and toxicological properties as well as the biodegradability of ionic liquids should have been thoroughly investigated. In addition, functionalized task specific ionic liquids (FTSIL) should be studies as they are capable of competing with alkanolamines in terms of solubility and rate of absorption.