

CHAPTER I

INTRODUCTION

Today, environmental issues such as climate change and global warming have been extensively burgeoning as global concerns due to emissions of green house gases (GHGs), especially carbon dioxide (CO₂), mainly from fossil fuel-based power generation. Another significant source of CO₂ is derived from produced natural gas found at the wellhead, which needs to be treated in gas sweetening plants to meet the heating value specification requirement and prevent the process equipment and pipelines from corrosion (Mortazavi-Manesh *et al.*, 2011). Moreover, many researchers have been focusing on the utilization of captured CO₂ in enhanced oil recovery (EOR), driving an interest in the development of technologies for efficient capture and sequestration of large quantities of CO₂. Currently, commercial CO₂ capture processes use aqueous amine solutions such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). These amine solutions are regarded as the most feasible option due to high CO₂ reactivity, low cost of solvents and high CO₂ absorption capacity. However, CO₂ absorption by the amines presents some drawbacks such as high energy consumption during regeneration, corrosiveness and vaporization losses (Ma'mun *et al.*, 2005). As a consequence, this left the door opened for research to find a more environmentally benign and energy-efficient CO₂ capture technology. Among the emerging technologies for CO₂ capture, ionic liquids have been widely considered, in recent years, as promising attractive candidates.

Ionic liquids are a class of organic salts that remains liquid at or near room temperature. In general, the structure of ionic liquids consists of a bulky asymmetric organic cation and either an inorganic or organic anion, making them solvents with low melting points (Marsh *et al.*, 2004; Laus *et al.*, 2005; Keskin *et al.*, 2007). Unlike conventional solvents, ionic liquids manifest a number of advantages determined by their unique physicochemical properties, such as negligible vapor pressure, high thermal stability, strong solubility capacity of CO₂ and tunability of structure and property. Owing to the negligibly low vapor pressure, ionic liquids as a more environmentally benign solvent have been suggested as a green alternative to

volatile organic compounds (VOCs) (Shin and Lee, 2008). A potential application of such organic salts is for gas separation processes including CO₂ capture. The non-volatile feature of ionic liquids would not cause any problem with respect to the contamination of the solvent to a gas stream, leading to a huge preference over other conventional solvents. Compared to the commercial amine processes, less solvent losses and lower energy consumption in the CO₂ absorption and regeneration process dealing with ionic liquids could be observed (Wappel *et al.*, 2010; Zhang *et al.*, 2012). It has been recently reported that CO₂ capture with 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) could reduce the energy losses by 16%, the investment by 11% and the equipment size by 12% (Shiflett *et al.*, 2010).

In order to select potential ionic liquids as absorption solvents for CO₂ capture, it is essential to know the solubility of the gas in the ionic liquid phase. Many research studies have been published on the solubility of gases in various ionic liquids. In literature, the most often found CO₂ solubility data are based on different imidazolium-based ionic liquids, especially 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) (Blanchard *et al.*, 2001; Anthony *et al.*, 2002; Camper *et al.*, 2004; Cadena *et al.*, 2004; Aki *et al.*, 2004; Camper *et al.*, 2005; Kim *et al.*, 2005; Anthony *et al.*, 2005; Shiflett and Yokozeki, 2005; Zhang *et al.*, 2005; Jacquemin *et al.*, 2006a; Kumelan *et al.*, 2006b), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) (Blanchard *et al.*, 2001; Husson-Borg *et al.*, 2003; Camper *et al.*, 2004; Cadena *et al.*, 2004; Aki *et al.*, 2004; Camper *et al.*, 2005; Anthony *et al.*, 2005; Shiflett and Yokozeki, 2005; Jacquemin *et al.*, 2006a; Chen *et al.*, 2006). However, reports on the solubility of CO₂ in ionic liquids containing other cations, such as ammonium (Anthony *et al.*, 2005; Jacquemin *et al.*, 2007; Muldoon *et al.*, 2007; Yuan *et al.*, 2007; Kilaru *et al.*, 2008; Kurnia *et al.*, 2009; Mattedi *et al.*, 2011; Manic *et al.*, 2012) and sulfonium (Blath *et al.*, 2011), have rarely been published. In this study, five conventional ionic liquids were selected based on the principle of their physical properties (i.e., liquid phase and low viscosity) and chemical structures consisting of potentially high-CO₂ affinity ions. Also, cost effectiveness is another important factor to be considered. Pertaining to the necessity of phase behavior studies, experimental gas solubility data for ionic liquids are, in general, available in a narrow region of thermodynamic variables including

temperature, pressure and composition. Appropriate thermodynamic models are essentially required to understand and predict the phase behavior of such systems.

In this research, the solubilities of CO₂ in five conventional ionic liquids: triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][Tf₂N]), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([deme][Tf₂N]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N]), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([amim][Tf₂N]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([4mbp][BF₄]) were measured using a gravimetric microbalance (IGA-003). The solubility measurement of this apparatus was based on the principle of weighing a sample bucket containing an ionic liquid before and after loading CO₂ at a fixed temperature and different pressures. Our experimental CO₂ solubility data in the investigated ionic liquids were compared to other ionic liquids published in literature. The experimental data for the binary systems of ionic liquid + CO₂ were correlated using theoretical cubic equations of state such as 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 (AspenPlus simulator). The adjustable binary interaction parameters, the Henry's law constants and the enthalpies and entropies of absorption for the studied ionic liquid + CO₂ systems were reported.