Fluid Phase Equilibria 385 (2015) 79–91

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Low pressure solubilities of CO_2 in guanidinium trifluoromethanesulfonate–MDEA systems

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ARTICLE INFO

Article history:
Received 17 May 2014
Received in revised form 24 October 2014
Accepted 5 November 2014
Available online 8 November 2014

Keywords:
Amine-functionalized ionic liquid
Guanidinium
Alkanolamine
CO_2 solubility
Physical property

ABSTRACT

It is an urgent act to limit greenhouse gas emissions to avoid the harmful effects of climate changes. In this work, the binary and ternary systems of guanidinium trifluoromethanesulfonate ([gua][OTf]) in *N*-methyldiethanolamine (MDEA) and/or water were examined as alternative solvents for gas treatment process. The thermodynamic properties including density, ρ, viscosity, η, thermal expansion, α_p and physical solubility of CO_2 in the systems were measured as a function of molar composition with a temperature range of 293.2–333.2 K at 100–1000 kPa. The presence of [gua][OTf] accelerates CO_2 absorption process. The present study offers equations of correlation providing a reliable prediction of the binary and ternary systems as a function of concentration. The linear equation, quadratic equation, extended Arhenius equation and Henry's Law equation have been applied to assess the validity of the finding. The CO_2 solubilities in [gua][OTf] systems are found higher compared to other ILs in previous researches. Additionally, ANN modeling of the effective parameters was carried out and the composition of [gua][OTf] was proven as the key factor in maximizing the CO_2 solubility.

1. Introduction

Amine scrubbing has been used to separate CO_2 from natural gas and hydrogen since 1930. It is a robust technology, well understood and widely used [1]. One of the most potent techniques widely used in capturing CO_2 from low pressure flue gas streams in power plants is chemical absorption using aqueous amine-based absorbents [2–4].

Furthermore, unprompted MDEA or alkali–carbonate solutions are very attractive as the solutions have high stability and are inexpensive [5]. The utmost benefits of MDEA are its high equilibrium loading capacity (about 1.0 mol of CO_2/mol of amine), the best selectivity under typical operating conditions encountered in the industry and low heat of reaction with the acid gases, which leads to lower energy requirement for regeneration [6–9]. On the other hand, MDEA has a low rate of reaction with (and therefore absorption of) CO_2. They are able to carry out a high total CO_2 removal, but at much lower rates [10–13]. Thus, new formulations comprising mixtures of amines with various additives are continuously being developed to overcome some of the drawbacks in their use and implementation.

It has been demonstrated previously that thermophysical properties have a substantial influence on the design of physicochemical processing and reaction units, especially the design parameters and performance of equipment like heat exchangers, distillation columns and reactors. To date, ionic liquids (ILs) have received an advantage in various applications including in CO_2 scrubbing [14–17]. ILs possess exceptional arrays of physical properties that make them suitable in numerous task-specific applications in which conventional solvents are ineffective, such as high heat capacity per unit volume, high thermal stability, high electrical conductivity, wide range of viscosity, very good solvent properties, and negligible vapor pressure [18–21].

Amine-based ILs as precursor liquids for CO_2 absorption was first discussed by Bates et al. [22] in 2002. Simple synthetic method and the use of commercially available starting materials are the highlight of this compound. However, the key problem of these task-specific ionic liquids (TSILs) is attributed to half-molar CO_2 uptake per one mole of IL. Likewise, the homogeneous ILs mainly suffers from gas diffusion limitation specially by increasing the viscosity of the CO_2-captured ILs. In our previous work, the solubility of CO_2 in aqueous blended system of MDEA and [gua][OTf] at partial pressure ranging from 500 to 3000 kPa were reported [23] . It has been found that the aqueous [gua][OTf] gave significantly higher solubility, up to 1.63 mol CO_2/mole absorbent, as compared to other pure ILs.

Abbreviations: IL, ionic liquid; [gua][OTf], guanidinium trifluoromethanesulfonate; MDEA, *N*-methyldiethanolamine; GC, gas chromatography; CO_2, carbon dioxide; ANN, artificial neural network.

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http://dx.doi.org/10.1016/j.fluid.2014.11.009
0378-3812/

Nomenclature

ρ	density
η	viscosity
α_p	thermal expansion
E_a	activation energy

Empirical equations for the density and viscosity of pure components as a function of a temperature and composition were applied and compared with experimental data. These equations are useful for interpolation within the studied temperature range. On the other hand, the excess thermodynamic properties and non-thermodynamic ones were fitted to a Redlich–Kister type equation using least squares to obtain their dependency on concentration and temperature [24–26]. A simple correlation is proposed in this work due to limited experimental data.

The complexities of parameters behavior in [gua][OTf]–MDEA systems for low pressure CO_2 solubility might cause misinterpretation of the results. The complexities cause major challenges for conventional methods such as one-variable-one-time [27]. CO_2 solubility does not depend on any single parameter alone and a combination of parameters affects the absorption of CO_2. An artificial neural network (ANN) is a powerful tool for analyzing this dependency. As consequence, ANN could be a promising multivariate method which involved complicated statistical calculation such as fitting process and regression analysis [28,29]. The ANN models possessed reliable, robust and salient characteristics in capturing the non-linear relationships between variables in the complex systems such as chemical reaction processes [30,31].

Hence, the objectives of this work are reported in four parts. Firstly, to contribute to the databank of physical property, by measuring the density, dynamic viscosity and CO_2 solubility of [gua][OTf]–MDEA systems. Secondly, to examine the effect of [gua][OTf] addition to MDEA as a function of temperature. Thirdly, to create a correlation of density, dynamic viscosity and CO_2 solubility in function of concentration (unit in M) of MDEA and [gua][OTf] at temperatures 298–363 K. Finally, to predict the most affecting parameter involving in CO_2 solubility by the development of a multilayer feed-forward neural network model, ANN.

2. Methodology

2.1. Chemicals

Analytical reagents (AR), [gua][OTf] and MDEA (98.5% and 98.0% by mass, determined by HPLC and GC, respectively), used in this work were purchased from Merck. The molecular formula, IUPAC name, CASRN, sources, purity grade, mass fraction and analysis method of the components are listed in Table 1. The structures of the [gua][OTf] and MDEA are shown in Fig. 1(a) and (b), respectively. The distilled water was used with double distilled purification. No further purification was made for all the compounds. Other chemical reagents include: HCl, $BaCl_2$, NaOH, $NaHCO_3$ and CO_2 were used without further treatment. Sodium hydroxide (NaOH, 99.0% purity), barium chloride ($BaCl_2$, 99% purity), and sodium bicarbonate ($NaHCO_3$, 99.0% purity) were purchased from Merck. Purified carbon dioxide (CO_2, purity $\geq$99.995%) was supplied by Malaysian Oxygen Berhad (MOX). Standard solution of hydrochloric acid (HCl, 1.0 N) for titration was obtained from Fisher Chemicals.

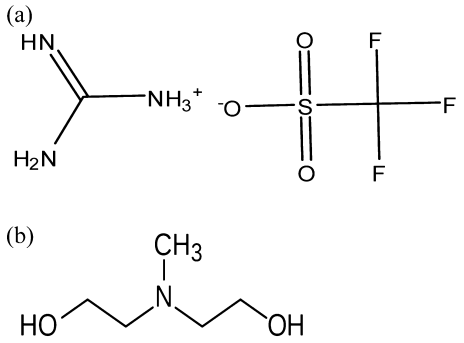

Fig. 1. (a) Structure of guanidinium trifluoromethanesulfonate, ([gua][OTf]) with molecular weight 209.15 g mol^{-1}. (b) Structure of *N*-methyldiethanolamine, (MDEA) with molecular weight 119.16 g mol^{-1}.

2.1.1. Sample preparation and validation

The compositions of the binary and ternary systems are shown in Table 2. All the systems were prepared gravimetrically and the accurate concentrations were determined by titration with 1.0 M HCl standard solution. All the systems used were found to be within 1% of the desired concentration.

2.2. Experimental setup and mode of operation

2.2.1. Density measurement

Density measurement of the binary and ternary systems was carried out with DMA- 4500 M (Anton Paar, Austria) digital densitometer thermostat at temperatures range of 273.2–363.2 K, with 10 K increment. The apparatus is precise within 1.0×10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than $\pm 1.0 \times 10^{-4}$ g/cm^3. The calibration of the densitometer was performed at atmospheric pressure using double-distilled and degassed water.

2.2.2. Viscosity measurement

Viscosity measurement was carried out using R/S+ rheometer (Brookfield, USA). The rheometer is a stress control (or controlled

Table 1
The sample provenance table for the compounds system.

Component	[gua][OTf]	MDEA
Molecular formula	$C_2H_6F_3N_3O_3S$	$CH_3N(CH_2CH_2OH)_2$
IUPAC name	Diaminomethylideneazanium; trifluoromethanesulfonate	2-[2-hydroxyethyl(methyl)amino]ethanol
CASRN	153756-25-3	511262-76-3
Source	Merck	Merck
Purity grade	AR	AR
Purity (mass fraction)	98.5	98.0
Purification method	None	None
Analysis method	HPLC	GC