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Absorption degree analysis on biogas separation with ionic liquid systems

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HIGHLIGHTS

- Thermodynamics and mass transfer properties were combined.
- A new criterion "absorption degree" was proposed.
- Absorption degree analysis is efficient for screening absorbents.
- The [bmim][NO_3] + NHD mixture is recommended for biogas separation.

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ABSTRACT

For biogas upgrading, present work mainly focuses on either thermodynamics or mass transfer properties. A systematical study on these two aspects is important for developing a new biogas separation process. In this work, a new criterion "absorption degree", which combines both thermodynamics and mass transfer properties, was proposed for the first time to comprehensively evaluate the absorption performance. Henry's law constants of CO_2 and CH_4 in ionic liquids–polyethylene glycol dimethyl ethers mixtures were investigated. The liquid-side mass transfer coefficients (k_L) were determined. The results indicate that IL–NHD mixtures exhibit not only a high CO_2/CH_4 selectivity, but also a fast k_L for CO_2 absorption. The [bmim][NO_3] + NHD mixtures present a high absorption degree value for CO_2 but a low value for CH_4. For presenting a highest relative absorption degree value, the 50 wt% [bmim][NO_3] + 50 wt% NHD mixture is recommended for biogas upgrading.

1. Introduction

The CO_2/CH_4 separation is the key procedure in the raw biogas upgrading process. The raw biogas, typically contains 53–70 vol% methane, 30–47 vol% carbon dioxide and some other trace compounds, is considered as an important renewable energy resource (Nie et al., 2013; Yan and Zheng, 2013). The raw biogas should be upgraded because the large amount of CO_2 greatly reduces the calorific value. After the upgrading process, the final product, bio-methane, can be injected into the pipeline grid as a source of energy (Shao et al., 2012). At present, absorption is one of the most widely applied technology for upgrading biogas (Zhao et al., 2013). Water and amine are the two representative absorbents for CO_2 capture (Scholz et al., 2013). For the water scrubbing process, the microbial growth on the surface of packing material and the low flexibility toward variation of input gas are the main drawbacks. In addition, water consumption is huge and the CO_2 cannot be recycled (Ryckebosch et al., 2011). Amines are the widely used chemical solvents which can enhance CO_2 absorption rate and capacity. However, the degradation of amine, the high energy consumption during regeneration and the loss of the amine are the common problems (Zhang et al., 2013).

Ionic liquids (ILs) have emerged as a new class of attractive solvents for gas separation because of their negligible vapor pressure, tunable physicochemical properties (Qu et al., 2014; Weerachanchai et al., 2012; Zhang et al., 2006, 2012b). It has been reported that the CO_2 solubility is much higher than the CH_4 solubility in ILs [bmim][Tf_2N] and [bmim][BF_4] (Mortazavi-Manesh et al., 2013; Raeissi and Peters, 2010). Therefore, ILs exhibit a high CO_2/CH_4 selectivity which can compete with the most commercial physical solvents (Althuluth et al., 2012; Anthony et al., 2002; Karadas et al., 2010). However, the main drawbacks of ILs are the relatively high viscosities and the high production costs. A new

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Nomenclature

List of symbols

a	specific gas–liquid interfacial area, $m^2\ m^{-3}$
A	gas–liquid interfacial area, m^2
C	concentration, mol m^{-3}
f	fugacity, kPa
H	Henry's constant, kPa
K_H	Henry's constant, Pa m^3 mol^{-1}
k_L	liquid-side mass transfer coefficient, m s^{-1}
k_La	volumetric mass transfer coefficient, s^{-1}
M	molecular weight, g mol^{-1}
n	mole amount, mol
N_A	overall mass transfer flux, mol s^{-1}
P	pressure, kPa
P^e	equilibrium pressure, kPa
P^0	initial pressure, kPa
P_{vapor}	vapor pressure, kPa
R	gas constant, J mol^{-1} K^{-1}
S	selectivity
t	time, s
T	temperature, K
V	volume, cm^3
x	mole fraction
Z	compressibility factor
$\Delta_{sol}H$	enthalpy of absorption, kJ mol^{-1}
$\Delta_{sol}G$	Gibbs energy of absorption, kJ mol^{-1}
$\Delta_{sol}S$	entropy of absorption, J mol^{-1} K^{-1}

Abbreviations

AD	absorption degree
IL	ionic liquid
NHD	polyethylene glycol dimethyl ethers
RAD	relative absorption degree

Greek letters

φ	fugacity coefficient
β	parameter

Subscripts

G	gas phase
L	liquid phase

approach to make ILs applicable in the CO_2/CH_4 separation system is to blend ILs with other commercially available solvents (Shannon et al., 2011). These mixtures can retain the desired properties of ILs but keep the viscosity relatively low as well as reduce the overall solvent costs. Polyethylene glycol dimethyl ethers (NHD), typically used for CO_2 physical capture, were selected to blend ILs to form hybrid absorbents. Compared with amines, the NHD has much lower vapor pressure and the NHD is non-corrosive to the equipment. However, the NHD also exhibits a relatively higher CH_4 solubility, which results in the lower CO_2/CH_4 selectivity (Rayer et al., 2012). It is expected that adding IL to NHD will enhance the CO_2/CH_4 selectivity of NHD and the IL–NHD binary mixtures will retain the properties for CO_2 capture but present a good CO_2/CH_4 selectivity.

In a gas absorption system, besides the thermodynamic properties, the mass transfer characteristics are very important for the suitable absorber design and the operation of industrial units. However, the mass transfer study on the gas absorption system with ILs is quite deficient, which cause a bottleneck in the large-scale application of ILs. In the previous works, the CO_2 bubble behaviors in IL systems have been investigated experimentally and numerically (Dong et al., 2010; Wang et al., 2010a,b; Zhang et al., 2014b, 2012a). The mass transfer characteristics of CO_2 chemical absorption by the blends of amine with ILs were reported by Zhang et al. (2014a), Ahmady et al. (2012) and Lu et al. (2013). But to the best of knowledge, there is a lack of information with regard to CH_4. The aim of this work is to consider both thermodynamics and mass transfer properties for optimizing the promising IL–NHD mixture for CO_2/CH_4 separation.

In this study, the CO_2, CH_4 solubilities and the CO_2/CH_4 selectivity in IL–NHD binary mixtures were investigated. The thermodynamic properties were calculated. The liquid-side mass transfer coefficients of CO_2, CH_4 in IL–NHD binary mixtures were determined from the fall in pressure, and effects of several operating parameters (i.e., different ILs, absorption temperature and IL concentration) on the Henry's law constant and the liquid-side mass transfer coefficient were evaluated. Taking both the thermodynamics and the mass transfer properties into consideration, a novel indication "absorption degree" was proposed.

2. Methodology

2.1. Absorption degree

To screen the desired absorbent for single gas absorption, both the thermodynamic properties and the mass transfer characteristics should be taken into consideration. Based on this idea, the new criterion "absorption degree" was proposed, and defined as follows:

$$\mathrm{AD} = \frac{k_L^i/H_i}{k_L^0/H_0} \tag{1}$$

where AD is the absorption degree, k_L^i, H_i are the liquid-side mass transfer coefficient and the Henry's law constant for the gas i in the absorbent, respectively. k_L^0, H_0 are the liquid-side mass transfer coefficient and Henry's law constant for the same gas i in the selected standard liquid.

Both k_L and H are influenced by the absorption temperature, therefore, the AD changes with absorption temperature. The AD can be calculated based on the values of k_L^i, H_i, k_L^0 and H_0 under the same absorption temperature. As for the selection of the standard liquid, it can be the specific liquid chosen in the experiments or some other liquid like water. It should be noted that the value of AD for the standard liquid at any temperature is 1. Here, the pure [bmim][BF_4] was chosen as the standard liquid.

Moreover, the AD should be combined with the selectivity when choosing the desired absorbent for two gases separation. According to this viewpoint, another similar criterion called "relative absorption degree" was proposed, defined as follows:

$$\mathrm{RAD}_{(i/j)} = \frac{k_L^i/H_i}{k_L^j/H_j} = \frac{k_L^i}{k_L^j}\frac{H_j}{H_i} = \frac{k_L^i}{k_L^j} \times S_{(i/j)} \tag{2}$$

where RAD is the relative absorption degree, k_L^i, H_i are the liquid-side mass transfer coefficient and the Henry's law constant for the gas i in the liquid. k_L^j, H_j are the liquid-side mass transfer coefficient and the Henry's law constant for the gas j in the same liquid. A high RAD value means that the absorbent is suitable for the two gases separation. Similar with the calculation of AD, each RAD data also