J. Chem. Thermodynamics 127 (2018) 71–79

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Below the room temperature measurements of solubilities in ester absorbents for CO_2 capture

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ARTICLE INFO

Article history:
Received 26 April 2018
Received in revised form 13 July 2018
Accepted 22 July 2018
Available online 23 July 2018

Keywords:
CO_2 solubilities
Henry's constant
Thermodynamic properties
Absorbents

ABSTRACT

Six ester absorbents were selected for CO_2 capture, such as methyl benzoate, methyl heptanoate, ethyl hexanoate, butyl butyrate, triethyl phosphate and tributyl phosphate. CO_2 solubilities in these absorbents were determined under temperatures of 273.15–283.15 K, and pressures up to 1.2 MPa. Henry's constants of CO_2 + the selected absorbent systems at 273.15 K and 283.15 K were calculated and compared with those at higher temperature. It seemed that decreasing the absorption temperature is obviously beneficial for enhancing absorption performance. In order to assess the absorption capacity for different physical absorbents, Henry's constants and volumetric solubilities of the selected absorbents were compared with ionic liquids, common solvents and the selected absorbents in our previous work. The result showed that tributyl phosphate and triethyl phosphate were found to be relatively good absorbents by mole and volumetric fraction respectively, and they have potential value for CO_2 capture. Moreover, thermodynamic properties such as entropy of solution, enthalpy of solution and Gibbs free energy of solution for the selected systems were calculated and assessed to study the absorption behavior.

1. Introduction

In recent years, carbon capture and storage (CCS) has been the effective technology for decreasing the release of excessive carbon dioxide into the atmosphere [1]. Currently, there are several methods as physical/chemical/hybrid absorption method [2], adsorption method [3–4], cryogenic method [5], membrane method [6] that are used to capture CO_2. Physical absorption method, which is mature and common in industry installations, is widely used under the condition of large amount of feed gas and extremely high CO_2 concentration. It is indicated that the development of new physical absorbent is one of the core parts for carbon capture technology [7].

Many researchers have concluded that different functional groups may lead to different CO_2 capacities for various physical absorbents. Gui [8] concluded that hydroxyl group may be considered as phobic-CO_2 group because strong hydrogen-bond interaction among the molecules of the absorbents may cause low solubilities of CO_2. In our previous work [9], carbonyl group is considered as philic-CO_2 group due to their good solvency for CO_2, which may be attributed to electronic theory of acids and bases. Strong interaction between carbonyl group (Lewis acid) and CO_2 (Lewis base) happens during the CO_2 absorption process. In addition, Perisanu [10] claimed that carbon dioxide shows very high solubilities in solvents containing carbon-oxygen bonds (esters, ethers, some ketones), which follows the principle "like dissolves like". Vapor-liquid equilibrium data of CO_2-various ester absorbents were determined, which showed the absorbents with ester groups showed excellent absorption behaviour. The solubility of carbon dioxide in six absorbents containing propylene carbonate (PC), ethyl carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and mixtures of these components were performed at temperatures from 275 to 333 K at atmospheric pressure by Blanchard [11]. It seemed that DEC was the best of the whole selected absorbents. Fandiño [12–13] reported CO_2 solubilities in four pentaerythritol esters as tetrapentanoate, tetra(2-ethylhexanoate), tetraheptanoate, tetranonanoate from (283 to 348) K and pressures up to 7.5 MPa. The result showed that in the present analyzed range CO_2 is highly soluble in these ester oils. Gui measured CO_2 solubilities in some esters as DMC [14], diethyl succinate [15], DMC + DEC [16], DMC + PC [16] and DMC + EC [16] at the temperature variations from 280 K to 313 K and pressures up to 6 MPa. Miller [17] assessed fifteen different low molar mass compounds including methyl acetate, 2-methoxy ethyl acetate, 2-(2-butoxyethoxy)ethyl acetate, PC, 2-butoxyethyl acetate as

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https://doi.org/10.1016/j.jct.2018.07.021
0021-9614/

Nomenclature

p_{CO2}	partial CO_2 pressure (MPa)
p_E	pressure of the equilibrium vessel after absorption (MPa)
p_v	vapor pressure of selected absorbents (MPa)
x_1	the mole fraction of liquid phase (-)
R	gas constant ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)
u	uncertainties of variables (the same as variables)
u_r	relative uncertainties of variables (–)
$H_x(T, p)$	Henry's constant based of mole fraction of CO_2 (MPa)
S	volume solubility of absorbent (cm^3 (STP)$\cdot cm^{-3}\cdot atm^{-1}$)
$\Delta_{sol}G$	Gibbs free energy of solution ($kJ{\cdot}mol^{-1}$)
$\Delta_{sol}H$	enthalpy of solution ($kJ{\cdot}mol^{-1}$)
$\Delta_{sol}S$	entropy of solution ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)

Greek letters

$f_1^L(T, p)$	CO_2 fugacity under desired temperature and pressure
$\phi_1(T, p)$	CO_2 fugacity coefficient under desired temperature and pressure

Subscripts

exp	experimental value
lit	literature data

CO_2 solvents based on the CO_2-solvent pressure-composition diagram at 298.15 K. When compared on a molar basis, 2-(2-butoxyethoxy)ethyl acetate rich with carbonate ester and ether groups was the best absorbent of the fifteen. Howlader [18] determined solubility of CO_2 in triglyaceride at different temperatures (283.2–303.2 K) and pressures (600–2450 kPa). Tian [19] and Cheng [20] measured CO_2 solubilities in ethyl propanoate, ethyl acetate, diethyl oxalate, ethyl laurate, and dibutyl phthalate at supercritical pressures. Moreover, Lenoir [21] determined CO_2 solubilities in the nineteen absorbents as alcohols, hydrocarbons, ketones, carbonate esters and phosphate esters at 298.15–343.15 K. Henry's constants of these solvents were reported and compared with each other, which indicated that phosphate esters showed relatively high absorption capacities of CO_2. In our previous work [9,22,23], the absorbents with carbonate ester groups such as ethylene glycol methyl ether acetate (EGMEA), propylene glycol methyl ether acetate (PGMEA), 3-methoxy butyl acetate (MBA), ethylene glycol butyl ether acetate (EGBEA) and carbitol acetate (CA) were selected, CO_2 solubilities in these absorbents were determined at the temperatures of 273.15–333.15 K and under pressures up to 1.2 MPa. The result showed that absorption capacities of these absorbents improve by 139–160% and 38–45%, with the condition of absorption temperature decreasing from 333.15 K to 273.15 K and from 293.15 K to 273.15 K respectively. Additionally, it is advantageous for decreasing circulation flow of the absorbent and minimizing the loss of absorbent. In this paper, the relatively low temperatures of 273.15 K and 283.15 K were chose to investigate CO_2 absorption properties of the physical absorbents.

Ester absorbents such as methyl benzoate, methyl heptanoate, ethyl hexanoate, butyl butyrate, triethyl phosphate, tributyl phosphate were selected to study the absorption behaviour at 273.15–283.15 K. Bamberger [24], Weng [25], and Chen [26] determined vapor–liquid equilibrium data of the CO_2-methyl benzoate system at supercritical pressure of 6.10–14.11 MPa, 3.0–14.5 MPa and 2.46–7.36 MPa, and under temperatures of 313.1–393.2 K, 313.15–348.15 K and 308.2–318.2 K respectively. Lenoir [21] measured CO_2 solubilities in triethyl phosphate and tributyl phosphate under the temperature of 325.14 K, and reported the results in the form of Henry's constants. In addition, Sweeney [27] reported Henry's constant of CO_2 for tributyl phosphate at 298.14–323.14 K. Vapor-liquid equilibrium data of the CO_2-ethyl hexanoate [28] system and the CO_2-tributyl phosphate [29] system at the temperatures of 308.2–328.2 K and 298.65–435.55 K were determined at supercritical pressure of 1.699–9.218 MPa and 8.42–27.51 MPa respectively. CO_2 solubilities in methyl benzoate, methyl heptanoate, ethyl hexanoate were determined at pressures up to 1.2 MPa and temperatures ranged from 293.15 K to 333.15 K, in our previous work that recently submitted to the journal of chemical thermodynamics [30]. There are no data on CO_2 solubilities in six absorbents under low pressures and 273.15–283.15 K that reported in the literature.

In this work, below the room temperature measurements of CO_2 solubilities in the six absorbents were made at 273.15 K and 283.15 K, and under pressures up to 1.2 MPa. Henry's constants and thermodynamic properties of the CO_2 + selected solvent systems were calculated and discussed.

2. Experiment

2.1. Materials

A Metrohm 831 Karl Fischer coulometer was used for the determination of the water content in the studied solvents. The purity that stated by the supplier, molecular structure, water mass fraction content, and source of the used chemicals are listed in Table 1. Ultra-purified water was used, which was produced by a Millipore water filtering system. In order to remove CO_2, water was boiled before use. The other substances were directly used without any further purification.

2.2. Apparatus

The device schematic with the isothermal synthetic method is shown in Fig. 1. CO_2 solubilities in various absorbents including physical [9,22,23,30] and hybrid [31] absorbents, were determined with the help of this device in our previous work. The device mainly consists of an equilibrium vessel, a gas chamber, a thermostatic-bath system, two pressure sensors, and a vacuum pump. The thermostatic bath provided by the refrigerator was used for temperature control of the two containers, with the assistance of a Julabo LC6 within the accuracy of ±0.03 K. Two pressure sensors (General Electric PTX5072), which are ranged up to 1500 kPa and with a precision of 0.2 kPa, were used for determining the pressures of the two containers. The densities of methyl benzoate [32], methyl heptanoate [33], ethyl hexanoate [32], butyl butanoate [34], triethyl phosphate [35], tributyl phosphate [35] were estimated by the extrapolations of the equations in the literature.

2.3. Experimental procedures

Initially, the whole system was evacuated by the vacuum pump. The physical absorbent was charged into the equilibrium vessel. The temperature of the thermostatic bath was set to the desired