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Solubilities of CO_2 capture absorbents methyl benzoate, ethyl hexanoate and methyl heptanoate

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ABSTRACT

Carbon capture, utilization and sequestration technology is effective for carbon emissions reduction. The development of new absorbent seems to be one of the core components of carbon capture technology. In this paper, three esters, methyl heptanoate, ethyl hexanoate and methyl benzoate, were selected to determine CO_2 solubilities at different temperatures ranging from 293.15 to 333.15 K, and pressures up to 1.2 MPa, using the isothermal synthesis method. The results showed that the absorbent with the straight-chain alkyl group was more effective for improving CO_2 absorption capacity than the benzene group. Ethyl hexanoate showed slightly higher CO_2 solubilities than its isomer methyl heptanoate. In addition, Henry's constant and thermodynamic properties such as solution enthalpy, solution entropy, solution Gibbs energy and solution heat capacity, were determined based on the measured data since the above properties are essential for designing an absorption process. Ethyl hexanoate is superior to the other two selected absorbents, common solvents, commercial absorbents, some physical absorbents, some polymeric absorbents and some ionic liquids, which indicates that it has potential value for CO_2 capture technology. However, further studies will be necessary to assess the reliability of its industrial application.

1. Introduction

In recent years, the greenhouse effect caused by the fossil fuel combustion has gradually endangered human survival [1]. CO_2 is considered as one of the main greenhouse gases and its emissions have increased year by year [2]. The International Energy Agency (IEA) indicated that carbon capture and sequestration (CCS) and carbon capture utilization (CCU) are potential technologies for the urgent need to reduce carbon emissions [3]. Separation methods for carbon capture are the physical/chemical/hybrid absorption method, adsorption method, cryogenic method and so on. The physical absorption method, which is mature and common in industry installations, is widely used under the conditions of large amount of feed gas and extremely high CO_2 concentrations. Methanol (MeOH), 1-methylpyrrolidin-2-one (NMP), poly(ethylene glycol) dimethyl ether (DEPG) and 4-methyl-1,3-dioxolan-2-one (PC) are physical absorbents for the Rectisol process, Purisol process, Selexol process and Fluor solvent process respectively. It is indicated that the development of new physical absorbents is one of the core issues in advancing carbon capture technology [4].

There have been various studies [5–26]——either experimental or predictive——carried out on new absorbents. Many studies [9–26] have focused on experimental determinations of the vapor-liquid equilibrium of CO_2 and physical absorbents. Miller [9] investigated phase behavior at 298.15 K for the binary systems of CO_2 and 15 volatile solvents such as propan-2-one, methyl acetate, *N*, *N*-dimethyl acetamide and so on. Solubilities of CO_2 in five levulinic acid-based deep eutectic solvents were reported by Deng [10] at T = (303.15–333.15)K. Siefert [11] presented the CO_2 pure gas solubility at 298.15 K and 313.15 K in the three solvents as polar ethylene glycol-siloxane-1 and so on. In our previous works [12–14], CO_2 solubilities in nine physical absorbents rich with carbonyl and ether groups such as 2-methoxyethylacetate, 3-methoxybutyl acetate, 2-(2-ethoxyethoxy)ethyl acetate and so on were determined at temperatures ranging from (293.15 to 333.15) K. Researchers tried to find the relationship between CO_2 capacity and the molecular structure of the physical absorbent based on the equilibrium data. Gui [15] concluded that the increase of hydroxyl groups in the absorbent molecule leads to the decrease of CO_2 solubility. The explanations are as follows. The absorption process between the gas and absorbent can be considered as two steps [15,27]: the molecular interactions among the absorbents are broken to form cavities; the gas enters the cavities, and the new interactions between the gas and absorbent molecules are

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List of symbols

p_{CO2}	partial CO_2 pressure (MPa)
p_t	the total pressure (MPa)
R	gas constant ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)
x_1	the mole fraction of CO_2 in the liquid mixture
u	uncertainties of variables (the same as variables)
$u_r(x_1)$	the relative standard uncertainties of CO_2 solubilities
$\triangle_{vap}H$	vaporization enthalpy ($kJ{\cdot}mol^{-1}$)
V	molar volume ($cm^3{\cdot}mol^{-1}$)
$H_x(T, p)$	Henry's constant based of mole fraction of CO_2 (MPa)
$\Delta_{sol}G$	solution Gibbs free energy ($kJ{\cdot}mol^{-1}$)
$\Delta_{sol}H$	solution enthalpy ($kJ{\cdot}mol^{-1}$)
$\Delta_{sol}S$	solution entropy ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)
$_{\Delta sol}C_p$	solution heat capacity ($kJ{\cdot}mol^{-1}{\cdot}K^{-1}$)

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
δ	solubility parameter (MPa^{-1})

Subscripts

exp	experimental value
cal	calculated value

created which shows the completion of absorption process. The decrease of CO_2 absorption capacity happens because more formation of hydrogen bonds among the absorbent molecules may lead to molecular interactions among the absorbents that are harder to break, as well as the creation of fewer cavities [28]. Li [13] and Kazarian [16] indicated that the absorbents with carbonyl and ester groups show excellent absorption behaviors for CO_2, which may be attributed to strong interactions between the electron acceptors and donors. Based on the electron theory of acids and bases, the carbonyl and ester groups may act as electron acceptors while CO_2 with lone electron pairs may be considered as electron donors. It turned out that the ester and carbonyl group in the absorbents may be called the CO_2-philic groups. Perisanu [29] claimed that carbon dioxide shows very high solubility in solvents containing carbon-oxygen bonds (esters, ethers, some ketones), which follows the principle "like dissolves like".

Henry's constants of the CO_2 + physical absorbents systems are always used for judging the absorption capacity of the absorbents. Li [17] calculated Henry's constant of CO_2 + poly (ethylene glycols) systems. Similarly, many other researchers [10,12,13,15,18–20] calculated Henry's constants of their selected absorbents for CO_2. Bara [30] compared Henry's constants of ionic liquids with commercial absorbents, and common solvents. Thermodynamic properties such as solution enthalpy ($\Delta_{sol}H$), solution entropy ($\Delta_{sol}S$), solution Gibbs energy ($\Delta_{sol}G$), and solution heat capacity ($\Delta_{sol}C_p$) are essential properties for the design of absorption process. Li [31] calculated the above four thermodynamic properties of ammonia + four basic imidazolium ionic liquids systems based on Henry's constants. Palgunadi [32] estimated the values of $\Delta_{sol}H$ $\Delta_{sol}S$ and $\Delta_{sol}G$ for the systems of CO_2 + dialkylimidazolium dialkylphosphate ionic liquids.

In this paper, methyl benzoate, ethyl hexanoate and methyl heptanoate were selected to study CO_2 absorption behavior. They are all with CO_2-philic groups, which makes them more competitive for CO_2 capture. Besides, they have excellent thermodynamic properties as thermal stability, moderate boiling point, non-corrosiveness, low viscosity and so on. There are no data about CO_2 solubilities in methyl heptanoate reported in the literature. Vapor-liquid equilibrium data of the CO_2-ethyl hexanoate system and the CO_2-methyl benzoate system at supercritical pressure were measured by Hwu [33], Weng [34], Bamberger [35] and Chen [36]. No data about the two above systems under low pressure were reported in the literature.

In this work, CO_2 solubilities in selected absorbents were determined at temperatures ranged from 293.15 K to 333.15 K and under pressures up to 1.2 MPa. Henry's constants and thermodynamic properties of CO_2 + selected absorbents systems were calculated and discussed.

2. Experimental section

2.1. Materials

The purity that stated by the supplier, CAS registry number, chemical structure, and source of the used chemicals are listed in Table 1. All of the substances were directly used without any further purification.

2.2. Apparatus

The device with isothermal synthesis method was used for determinations of CO_2 solubilities in physical [12,13,37] and hybrid [38,39] absorbents in our previous works. It has been used directly for the determinations of selected absorbents without any modification. The sketch map of the device is presented in Fig.1. The device mainly consists of a gas chamber and an equilibrium vessel, whose volumes were 332.89 mL and 1031.3 mL respectively. A Julabo LC6 within the accuracy of ±0.03 K, was used for temperature control of the two containers with the help of a water bath. The pressures of the two containers were monitored by two PTX5072 sensors (General Electric) with the precision of 0.2 kPa. Densities and vapor pressures of ethyl hexanoate [40,41] methyl benzoate [40,42] and methyl heptanoate [43,44] were obtained in the literatures.

2.3. Experimental procedures

Initially, the air from the pipes and the two containers was removed with the vacuum pump, and about 25 mL of physical absorbent was charge into the equilibrium vessel with the burette. Then the Julabo LC6 should be set to the desired temperature in order to maintain the temperatures of two containers. The pressures of two containers were recorded after the temperature became constant. Some CO_2 from the gas chamber was charged into the equilibrium vessel. The gas-liquid equilibrium of CO_2-absorbent system was established when there wasn't any possible change of pressure in the equilibrium vessel. CO_2 solubilities(x_1) and their relative standard uncertainties ($u_r(x_1)$) were calculated according to our previous work [37].

2.4. Apparatus reliability validation

In our previous work [12], CO_2 solubilities in NMP at 298.15 K and under pressures up to 1.5 MPa were determined and compared with the data in the literature [45], which meant that the device was accurate and reliable.