

Comparative study: Absorption enthalpy of carbon dioxide into aqueous diisopropanolamine and monoethanolamine solutions and densities of the carbonated amine solutions



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ABSTRACT

Absorption processes using aqueous alkanolamines are under intense research for new gas purification and carbon capture applications. In this work continuous flow calorimetry (SETARAM C80) and vibrating tube densimetry were used to measure absorption enthalpies of carbon dioxide (CO₂) into aqueous amine solutions and the final densities of carbonated amine solutions. We present new data for monoethanolamine (MEA) and diisopropanolamine (DIPA) solutions of 0.1–0.2 mass fraction MEA and 0.1–0.3 mass fraction DIPA. CO₂ loadings used in the study were 0–1.0 mol CO₂/mol amine. New experimental data presented herein will facilitate the validation and/or further development of thermodynamic models describing the absorption phenomena.

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1. Introduction

Aqueous alkanolamines have long been used in industrial sour gas removal applications, especially in natural gas purification. Monoethanolamine (MEA) and diisopropanolamine (DIPA) are common industrial solvents in the purification of natural and synthesis gases [1]. Increased interest in carbon capture and sequestration (CCS) technologies, and removal of carbon dioxide from flue gases has further intensified the research on alkanolamines. The development of any new process, or re-engineering of an existing one for a new application, is greatly facilitated by accurate process simulations, which in turn rely on accurate thermodynamic data.

Liquid chemical absorbents are commonly used in CO₂ removal from gas streams, due to their strong absorbing capacity. Compared to most physical solvents, chemical solvents can achieve more complete CO₂ removal [2]. One drawback of the chemical absorption process is the higher energy requirement for the regeneration of the absorbent solution. The regeneration step contributes to a considerable portion of the operating costs of a gas treatment process. Total energy consumption of an amine

regeneration process can be divided into contributions from the heat required to heat the incoming flow to regenerator temperature, the heat used to generate the stripping stream and the heat needed to release the chemically bound CO₂ from the solvent [3]. CO₂ absorption/desorption heat is thermodynamically linked with the absorption capacity of the CO₂ absorbing solvent. Mathias et al. [4] demonstrated that by choosing a chemical absorbent with appropriate CO₂ absorption capacity and enthalpy of CO₂ absorption, heat duties of regeneration processes can be lowered.

Aqueous solutions of MEA are widely used as chemical absorbents for sour gases, particularly for CO₂, but its use is hindered by large regeneration energy requirement. Weiland et al. [5], have measured the density of carbonated MEA solutions of 0.1–0.4 MEA mass fraction (w_{MEA}), with CO₂ loadings up to 0.25 mol CO₂ (mol MEA)⁻¹. Amundsen et al. [6], have measured carbonated MEA solution densities for $w_{\text{MEA}} = 0.2\text{--}0.4$ with CO₂ loading of 0–0.5 mol CO₂ (mol MEA)⁻¹. Han et al. [7] have reported densities of MEA solutions with 0.4–1.0 MEA mass fraction and 0–5 mol CO₂ (mol MEA)⁻¹. They also extended the range of the density correlation developed by Weiland et al. [5], to cover solutions with higher MEA content.

Absorption enthalpy of CO₂ is usually given either as differential or integral heat of absorption. Integral heat of absorption is the molar heat evolved when pure amine solution ($\alpha = 0$) absorbs certain amount of CO₂. Differential heat of absorption corresponds to

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Nomenclature

Roman letters

a, b, c, d	regression coefficients of Weiland equation (Eq. (7)–(9))
E	calorimeter sensitivity, $W \mu V^{-1}$
G	Gibbs free energy, $J mol^{-1}$
H	enthalpy, $J mol^{-1}$
K	equilibrium constant, mole fraction based
m	mass, g
\dot{m}	mass flow, $g s^{-1}$
\dot{n}	molar flow, $mol s^{-1}$
P	pressure, Pa
R	gas constant, $J (K mol)^{-1}$
S	calorimeter signal, μV
T	temperature, K
u	standard uncertainty
U	expanded standard uncertainty
V	molar volume, $cm^3 mol^{-1}$
\dot{V}	volumetric flow, $m^3 s^{-1}$
w	solution mass fraction before CO_2 absorption
x	liquid phase mole fraction
Z_{CO_2}	CO_2 compressibility

Greek letters

α	CO_2 loading, $mol CO_2 (mol amine)^{-1}$
γ	activity coefficient
ν	stoichiometric coefficient
τ	vibrational period

Sub- and superscripts

$^\circ$	standard state
ABS	absorption
Am	amine, MEA or DIPA
E	excess property
C	combined (uncertainty)
i	order number for a component
j	order number for a reaction
r	reaction
R	relative (uncertainty)

the heat evolved when infinitesimal amount of CO_2 is absorbed by a solution containing known loading of CO_2 . If experimental measurements for the heat of solution are not available, differential heat of absorption can be successfully evaluated from solubility data [8] but this derivation procedure can also lead to increased uncertainty of the obtained values [9]. Experimentally determination of differential heat of absorption is more complicated than determination of integral heat of absorption, but some measurements have been published e.g. by Carson et al. [10], and Kim and Svendsen [9]. Among others Mathonat et al. [11], and Arcis et al. [12], have reported calorimetrically measured integral absorption enthalpies of CO_2 into MEA. These measurements have mostly been conducted at temperatures of 313 K or above and typically for $w_{MEA} = 0.3$. Carson et al. [10], have reported enthalpy data at 298.15 K for solutions with $w_{MEA} = 0.1–0.3$, but at very limited CO_2 loading range.

Solutions of DIPA, another industrially interesting alkanolamine, have been reported as less corrosive and energetically cheaper to regenerate than MEA [1]. Previously Dell'Era et al. [13], have reported VLE and density data for DIPA– H_2O – CO_2 –system. Only limited data exist on enthalpy of CO_2 absorption into DIPA solutions. Kohl and Nielsen [1] report an approximate value for the integral heat of absorption averaged from operating data of

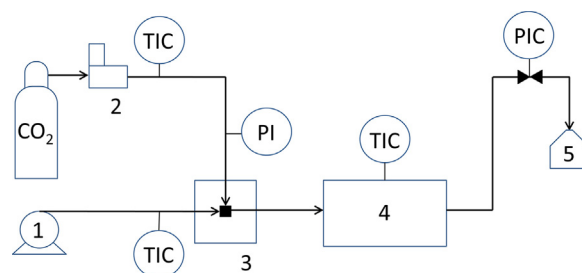


Fig. 1. Simplified experimental setup, (1) amine solution pump, (2) CO_2 regulation (mass flow controller or ISCO syringe pump), (3) SETARAM calorimeter, (4) density meter, (5) waste collection.

industrial processes of $-74 kJ (mol CO_2)^{-1}$ at 311 K, for the CO_2 loading of approximately $0.4 mol CO_2 (mol DIPA)^{-1}$.

Excess Gibbs energy based activity coefficient models have been applied extensively for the modeling of CO_2 solubility in aqueous alkanolamines [14–19]. Zhang et al. [18], have used electrolyte Non-Random Two Liquid model (eNRTL) to model the CO_2 absorption in aqueous MEA. Zong and Chen [19] have used the same thermodynamic framework to model sour gas absorption in aqueous solutions of DIPA, methyldiethanolamine (MDEA) and sulfolane. These models were chosen to be compared against the measured enthalpy data, in order to evaluate the predictive capabilities of existing thermodynamic models.

In this work new density data was measured for carbonated DIPA solutions, extending the work done by Dell'Era et al. [13], to a larger loading range with CO_2 loadings from 0 to $1 mol CO_2 (mol DIPA)^{-1}$. New integral absorption enthalpy data of this work for aqueous MEA at 298 K extend to much higher CO_2 loadings than previously reported e.g. by Carson et al. [10]. The integral absorption enthalpy data for CO_2 into DIPA measured in this work are considered especially valuable, since there are no such enthalpy measurements in the scientific literature. Experimental data were compared to previous measurements, and to the modeled results from Zhang et al. [18], and Zong and Chen [19].

2. Experimental

2.1. Materials

Chemicals used in this work were monoethanolamine and diisopropanolamine. Both were purchased from Sigma–Aldrich, and they were used as received without any additional purification. Carbon dioxide was obtained from AGA. Purities of the used compounds are shown in Table 1. Pure water for the aqueous solutions was produced in the laboratory with our Millipore Elix 20 water purification system. Aqueous amine solutions were prepared by weighing the appropriate amounts of amines and water with a laboratory scale accuracy of $\pm 1 mg$.

2.2. Equipment

The experimental setup is shown in Fig. 1. The setup used in this work allowed simultaneous measurement of carbon dioxide absorption enthalpy and of the density of the carbonated amine solution. The CO_2 absorption enthalpies were measured with Setaram C80-calorimeter [20] equipped with a flow through mixing cell. Setaram C80-calorimeter has an internal temperature measurement and control system for the control of measurement temperature with accuracy of $\pm 0.1 K$. A similar calorimeter has been successfully employed by Arcis et al. [12], for the determination of CO_2 absorption enthalpies.

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