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Gas solubilities of carbon dioxide in methanol, acetone, mixtures of methanol and water, and mixtures of methanol and acetone

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ABSTRACT

Although a lot of investigations have been performed on solvents regarding the absorption of CO_2 in the past decades, not much is known about absorption in mixtures of solvents. It is supposed that additives like acetone lead to higher CO_2 solubilities in methanol compared to absorption in pure methanol. Moreover, there is very little information on the absorption of CO_2 in methanol with contents of water, which is present in many absorption processes. In this work, a new apparatus is introduced for the investigation of gas solubilities in physical solvents like alcohols, ketones or other solvents in a temperature range of $T = 253.15$ K to $T = 453.15$ K. Two different measurement methods are shown and the results are published as (p, x) data and diagrams. The obtained data increase the knowledge of solubilities of CO_2 in mixtures of methanol and water at certain water contents as well as in acetone at temperatures of $T \ll 298.15$ K, which have not been examined in modern, accessible literature before. The absorption of CO_2 in mixtures of acetone and methanol is published for the first time.

1. Introduction

A major task of the ongoing 21st century is the reduction of carbon dioxide (CO_2) emissions, which cause the so-called greenhouse effect [1]. One of the large sources of emissions can be found in industry and in the production of electricity and heat, which is mainly based on fossil fuels [2]. A major topic in the past years has been the concept of carbon capture, where carbon dioxide is separated from flue gas streams. This can be done in different technological ways, for example via biological routes [3,4] or adsorption processes [5]. However, carbon dioxide is not only a greenhouse gas, it is often used as a valuable chemical for a large number of processes. Therefore, it is very important to either produce large amounts of usable pure carbon dioxide or to design processes that are more or less emission-free.

The focus of this work is the absorption of CO_2 in physical solvents like alcohols and ketones. Industrial absorption processes are often operated with solvents that have to match different criteria, which include economical costs, low toxicity, easy regeneration in desorption processes, long term stability and high solubility of the gas in the solvent. One focus of improving absorption processes is minimizing the energy demand necessary for the regeneration. This can be done by mixtures of solvents and the use of additives to well-known solvents [6].

A very good overview of different ways of measuring phase equilibria, which include the gas solubility in the solvent and the knowledge of the evaporation of the solvent, can be found in Ref. [7]. Many different solvents have been investigated in the past and their ability for CO_2 absorption processes has been analyzed. One of the most common solvents in industry is used in the Rectisol® process, in which gas is cleaned by methanol (MeOH) as a solvent [8]. Although the solubility of CO_2 in methanol has been widely studied [9–15] the difference in solubilities in literature sources, especially at high pressures, is significant. Often, no uncertainties of the measured values are given or the presented uncertainties are estimated to be very low. The reliability of these values cannot be evaluated completely. This may lead to the conclusion that at least some of the published results have to be doubtful. Most data are available at a temperature of $T = 298.15$ K, which is supposed to be the standard condition of gas solubility measurements because of the ease of access. Therefore, the system CO_2/MeOH is suitable for the validation of new experimental setups.

An important aspect is the solubility of CO_2 in solvents like

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methanol in the presence of water (H_2O). In many gas cleaning processes like CO_2 absorption from flue gas or the processing of hydrogen (H_2), a vapor-liquid phase equilibrium of the components CO_2, H_2O and the solvent is present in the absorber columns. The gas solubility of H_2 in the solvent is very low and therefore, this component can be neglected for equilibria investigations. For the design of absorption units, precise knowledge of the vapor-liquid equilibrium is essential. Only few data can be found in the literature for the system CO_2/MeOH/H_2O [9,16–18].

The gas solubility of CO_2 in acetone (Ac) is also well reported in the literature. Most authors have published data at temperatures of $T = 298.15$ K or higher [19–24]. Only a few data sets can be found for mixtures of different solvents. In the case of methanol containing amounts of acetone, no values are available in the literature.

Besides theoretical investigations on physical properties of chemical compounds and theoretical approaches on absorption processes [25], experimental determination of properties is an important aspect in thermal process engineering. This work expands the knowledge of gas solubility in physical solvents and their mixtures and shows the influence of low water contents on the gas solubility of CO_2 in methanol.

2. Experimental

2.1. Material

The used chemicals are presented in Table 1. All purities given are based on manufacturers' information and chemicals were used without further treatment.

2.2. Apparatus

A new apparatus for the measurement of phase equilibria and gas solubility was developed, designed and constructed [26]. The set-up was inspired by the work of Fonseca et al. [27] where an apparatus for measuring phase equilibria was presented for systems containing hydrocarbons, water and hydrate inhibitors [27]. A major difference between that apparatus and the one described in this work is that an equilibrium cell was used without the possibility of changing the height of the gas-liquid interface. As only gas solubilities in the liquid were to be investigated, the height of the liquid filling level did not have to be movable. Therefore, a fixed height of the sample taking was sufficient. In Fig. 1, an overview of the experimental set-up is shown. The main part of the apparatus is a stainless steel equilibrium cell with a total volume of $V = 366$ ml. For constant isothermal conditions, the cell was placed inside a temperature chamber for a temperature range of $T = 253.15$ K to $T = 453.15$ K. The apparatus was designed for pressures up to $p = 75$ bar. Liquid and gas could be fed into the equilibrium cell through the supply pipes. Borosilicate glass at the front and back sides of the equilibrium cell offered the possibility of investigating the interface of gas and liquid. A stirrer plate in combination with a magnetic stir bar was used for achieving a rapid equilibrium indicated in constant values of temperature and pressure. For the temperature measurement, several Pt100 sensors were used with an estimated accuracy of ±0.1 K. The pressure was detected with the *PM-33X* sensor by *KELLER Ges. für Druckmesstechnik mbH* and with an accuracy of ±0.1 bar (manufacturer information). Three electromagnetic ROLSI™ (Rapid On-line Sampler-Injector, further development of [28]) were installed on the right side of the apparatus. The liquid or gaseous sample flowed throw a thin capillary (diameter $d = 0.13$ mm) for a controlled period of time into the stainless steel body of the ROLSI™ system. The sample was evaporated in the heated body and fed into the carrier gas stream of the gas chromatograph (DANI Master GC), where it was analyzed.

Table 1
Chemicals used in the experiments.

Chemical	Purity	Supplier	$\overline{M}$ in $\frac{kg}{kmol}$
CO_2	99.995 vol%	*Rießner-Gase GmbH, Germany* *Westfalen AG, Germany*	44.01
Methanol	99.9 wt%	*Carl Roth GmbH + Co. KG, Germany* *Merck KGaA, Germany*	32.04
Water		demineralized and bidestilled	18.02
Acetone	99.8 wt%	*Merck KGaA, Germany*	58.08

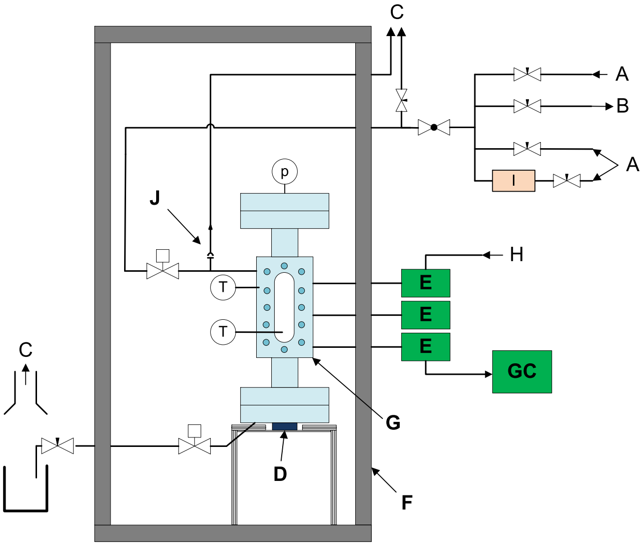

Fig. 1. New apparatus for the measurement of gas solubilities in physical solvents. **A**: gaseous and liquid supply, **B**: vacuum, **C**: vent, **D**: stirrer plate, **E**: ROLSI™, **F**: temperature chamber, **G**: equilibrium cell, **H**: carrier gas to gas chromatograph (**GC**), **I**: gas cylinder, **J**: rupture disc, **p**: pressure sensor, **T**: temperature sensor.

2.3. Measurement methods

Two measurement methods are presented in the following. The main difference between these two routes is the measurement with or without sample taking, which are an *Analytical* and *Synthetic Method*, respectively.

Analytical method

As only the ratio of components to each other was needed for the mole fraction x_{CO_2} of carbon dioxide in the liquid phase, the total amounts did not need to be known. Therefore, it was not necessary to know the exact amounts of the components fed into the equilibrium cell at the beginning of the experiment. In general, with this experimental set-up, up to three ROLSI™ could be used for sample taking at different heights of the cell or phases. Since only gas solubilities in the liquid phase were examined in this work, only the ROLSI™ at the bottom outlet was used (cf. Fig. 1). The GC was calibrated with known amounts of the components of interest with the use of gastight syringes. Thereby, a polynomial correlation could be found between the detected peak area A_i and the mole amount N_i of the component i. The coefficients of the correlations were found by a modified least square method. In this *Analytical Method*, the sample taking was performed via the pressure difference between the pressure in the equilibrium cell and the carrier gas line of the gas chromatograph. Therefore, a minimum pressure of approx. $p = 5$ bar in the equilibrium cell had to be considered. Every equilibrium state was measured several times. In order to