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Basic Solubility Measurements for the Design of an Integrated Biogas Purification Process

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Basic solubility measurements have been carried out in order to investigate the co-solubility of carbon dioxide (CO_2) and methane (CH_4) in water at 298.15 K. Since there is no publicly available solubility data for moderate pressures (as applied in pressurized water scrubbing) for the removal of carbon dioxide from biogas, mixed gas solubilities subject to pressures of approximately 0.2 MPa to 1.5 MPa were investigated using a self-designed equilibrium cell. Since CO_2 and particularly methane are only sparsely soluble in water, a precise method had to be developed for measuring the dissolved amount of both solutes at various pressures. Additionally, reference measurements with pure solutes were completed and compared to existing literature data for the respective solutes to validate the method of measurement. The results show a good agreement with the literature data. An influence of the dissolved CO_2 on the solution behaviour of methane was found. The solution equilibrium is analysed by fitting the data to the Krichevsky-Kasarnovsky-Equation of Henry's Law.

1. Introduction

Upgrading biogas to bio natural gas is a promising way to substitute regenerative biogas for fossil natural gas in the long run. Besides some trace substances, biogas basically consists of methane and carbon dioxide. To produce bio natural gas, the latter has to be removed from the biogas stream. This is necessary since the physical properties of bio natural gas have to comply with the requirements and regulations of natural gas, e.g. the heating value, before blending it into the existing natural gas grid. There are several different commercially used processes for this upgrading step e.g. amine scrubbing, pressure swing adsorption, pressurized water scrubbing and, recently increasing, membrane separation processes (Reppich et al., 2009). The removal of CO_2 is the most complex and energy intensive upgrading step for the biogas purification (Urban et al, 2009). Classic separation processes are technically mature without making use of synergies between the respective process units. Membrane processes, however, have a high potential to lower separation costs due to their alleged simple operation. However, they lack high separation efficiencies thus, their combination with other unit operations is useful. (Bernardo et al, 2009). In this work, a novel hybrid membrane absorption cell is designed based on experimentally determined data. The combination of a dense polymer membrane and pressurized water as a scrubbing solution combines the advantages of the simple unit operations absorption and gas permeation. i.e. a very high area to volume ratio and a high selectivity for the hybrid process. The absence of hazardous or caustic scrubbing agents accomplished by the use of pure water as a scrubbing solution accounts for a possible application on farms. The process is designed to promote a sustainable, robust and environmentally friendly process. Since the published data on the co-solubility of methane and carbon dioxide in water at moderate pressures is very limited, a test cell

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has been constructed for measuring the influence of the dissolved CO_2 on the methane solubility. This data is necessary for the exact design of the hybrid membrane absorber.

1.1 State of the Art

There is a long history of gas solubility measurements in water and considerable amounts of data are reported for various conditions. For CO_2 and CH_4, such data are available in the form of single-gas solubilities in water, aqueous solutions, electrolyte solutions and organic solvents (Clever and Young,1987), (Scharlin, 1996). In particular, the system CO_2-water has been thoroughly investigated. Carroll et al (1991) published an excellent revue on the solubility of CO_2 in water. Since the solubility of methane in water is very low, precise measurements of the methane-water system are rare. Nevertheless, profound data on the system CH_4-water can be found at 298.15 K in the considered pressure range (Duffy et al. 1961; Rettich et al. 1981; Fogg 1991). Few data are published on the co-solubility of CO_2 and methane in water. In fact, there is little data to be found on the co-solubility of gases in a single solute in general. To the best of our knowledge, there were no data found for the pressure range that is considered in this paper. Zhang et al. (2004) did measurements on CO_2-CH_4 mixtures in water, however, they studied the solubility near hydrate conditions. It is generally said that the solutes do not interact with each other, especially if the concentration in the solvent is low and if there is no chemical reaction between the solute and the solvent. Pure gas solubilities of the respective solutes can be used to describe the gas-liquid equilibrium of the mixed gas interacting with the solvent (Sattler and Adrian, 2007). Nevertheless, it is known (Stoessel and Byrne, 1981) that bicarbonate (HCO_3^--) ions create a salting-out effect that affects the solubility of other solutes. These bicarbonate ions are formed by the dissociation of H_2CO_3 in water. Particularly at higher pressures and increased CO_2-solubility, the amount of bicarbonate ions affects the solubility of methane in water. This must be considered in the design of an absorption process. The effect is even more pronounced when an electrolyte solution is being used as a solute since the dissociation reaction favours the formation of bicarbonate ions at a higher value of pH. By adding acidic substances to CO_2, the salting out effect can be enhanced.

2. Experimental Setup

A novel test cell has been designed in order to precisely measure the co-solubility of gases in liquids for pressures up to 1.5 MPa at different temperatures. Measurements were carried out for the systems CO_2, CH_4 and CO_2-CH_4 in water at 25°C. The basic setup is shown in Figure1.

2.1 Materials

Purified water (conductibility resistance > 18 MΩ) that was degassed thoroughly was used in all experiments. The purified water was degassed while evacuated to 3 kPa and heated to 40 °C in an ultrasonic water bath. Pure CO_2 (99.995 %) and pure CH_4 (99.2 %) were used for the single-gas reference measurements. Gas mixtures containing 50 vol% CH_4 and 60 vol% CH_4 were used for the mixed-gas solubilities since they represent typical biogas compositions. All gases were purchased from Praxair Germany and were certified to have an accuracy of $2\%_{rel}$.

2.2 Apparatus

The pressure-tight test cell has an inner volume of 362.52 ml and is made of stainless steel. A precise pressure meter (0.1 % FSO 0-16 bar) was used to measure the absolute pressure in the cell. The quantity of gas that was necessary to reach the initial pressure was measured using a thermal mass flow controller (Bronkhorst EL-Flow 200). For pure gas measurements, this is exactly the quantity of gas dissolved in water in equilibrium since the pressure at the non-dissolved state equals the pressure after the equilibrium is reached. For gas mixtures, the change in the composition of the gas phase was analysed using a GC TCD (Perkin Elmer). The temperature in the cell was kept constant at 298.15 K and was measured in the liquid and in the gas phase via resistance thermometers (PT 100 precision 1/10 B). The whole cell was kept at constant 298.15 K (±0.01K) in a water bath. The solute was stirred continuously using a magnetic stirrer (100 U/min).

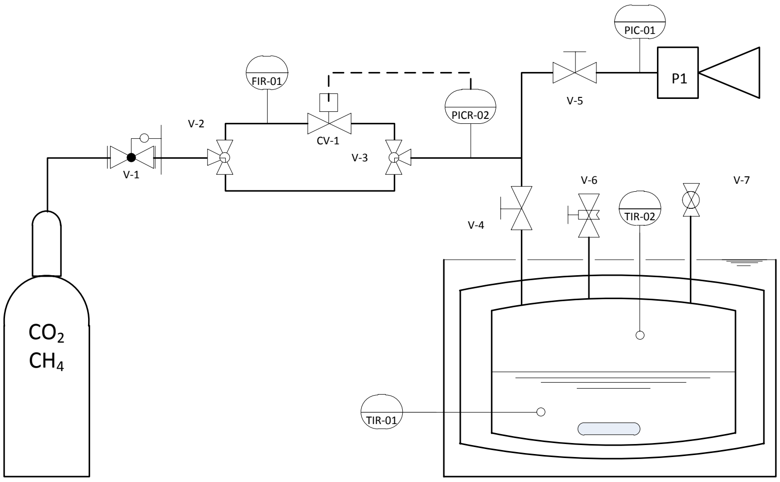

Figure 1*: Set-up of the complete test cell*

2.3 Procedure

The test cell was flushed twice with the gas mixture and evacuated to p_0< 4 kPa using a water jet pump. A certain amount of degassed purified water (around 200 mL) was injected into the test cell and tempered to 298.15 K. The test gas pressure reducer was set to the desired pressure and the gas was quickly introduced into the test cell for 15 s. The pressure and temperature of this initial state was noted. It was assumed that during the introduction, no relevant amount of gas had dissolved in water since the stirrer was not activated, i.e. the mass transfer resistance was significantly high. The gas-liquid equilibrium developed under continuous stirring while the entering rebalance gas was fed through the flow meter. A feed-back flow controller adjusted the flow in order to reach the initial pressure. After the temperature and pressure reached their initial values and the system is in equilibrium, the gas phase concentration was analyzed and compared with the initial concentration. The amount of dissolved gas could then be calculated.

3. Results and Discussion

The apparatus was designed for determining pure and mixed gas solubilities in liquids. For pure gases, it is not necessary to use any equation of state like for some other methods (Hefter, 2003). The solubility can be measured directly without any assumptions or simplifications.

Table 1: Pure gas solubilities and literature references (linear interpolated) for CO_2-H_2O

Partial pressure	MPa	0.3228	0.4963	0.7032	0.8873	1.0837
Own measurements	x*1000	1.945	2.952	4.251	5.037	6.147
Accuracy	%	1.3	0.6	-	2.2	8.5
Literature (Houghton, 1957)	x*1000	1.798	2.764	3.916	4.941	6.034
Percent Error	%	7.6	6.4	7.9	1.9	1.8

Table 2: Pure gas solubilities and literature references (linear interpolated) for CH_4-H_2O

Partial pressure	MPa	1.1372	1.4301
Own measurements	x*1000	0.2286	0.3077
Accuracy	%	1.6	0.7
Literature (Duffy,1961)	x*1000	0.2522	0.3171
Percent Error	%	10.3	3.1

For mixed gases it is necessary to correct the gas phase from the initial state to the final state in equilibrium since the gas phase composition changes although the pressure in both states is the same. By the use of an equation of state it is possible to calculate the amount of dissolved CO_2 and CH_4 by measuring the amount of gas that is necessary to compensate for the pressure decrease in the test cell caused by absorption. In Table 1 and 2 the experimental results are summarized and compared with literature data.

3.1 Feed gas analysis

The pVT-behaviour of a mixture consisting of a polar and a non-polar gas can be described using the Lee-Kesler-Plöcker equation of state (Plöcker et al.,1978). The real gas factor z is calculated for the initial and final temperature, pressure and composition, respectively (1). The amount of moles that entered the test cell via the bypass and the amount of moles in the equilibrium state can be calculated using equation 2 and a simple mass balance (3) is used to calculate the moles dissolved.

$$z = z(p,T,y) \tag{1}$$

$$n = \frac{pV}{zRT} \tag{2}$$

$$n_i^{diss} = n_i^{G,0} + n_i^{add} - n_i^{G,\infty} \tag{3}$$

The measured gas flow is integrated using equation 4:

$$n^{add} = \int_{t=0}^{t\infty} \dot{n}^{add} dt \tag{4}$$

The gas phase concentration y_i is determined using a GC.

$$n_i = y_i n \tag{5}$$

Henry’s law describes the solubility of gases in liquids. As described by Carroll (1991), the definition of the Henry’s constant is

$$\lim_{x_i \to 0} \frac{f_L^i}{x_i} = H_{ij} \tag{6}$$

For low solubilities, moderate pressures and a constant temperature, Henry’s law is a linear function of pressure. For higher pressures, the Krichevsky-Kasarnovsky-Equation (7), which takes into account the pressure influence on solubility, has to be used. This equation is useful for systems where the solubility remains low ($x_i < 0.01$) even at higher pressures (Carroll, 1991).

$$\ln \frac{f_i^V}{x_i} = \ln H_{ij} + \bar{v}_i^\infty \frac{(P-P_j^0)}{RT} \tag{7}$$

The vapour phase fugacity is calculated using Lee-Kesler-Plöcker equation of state and Henry’s coefficient is given by the slope of the straight lines in Figure 2 and Figure 3.

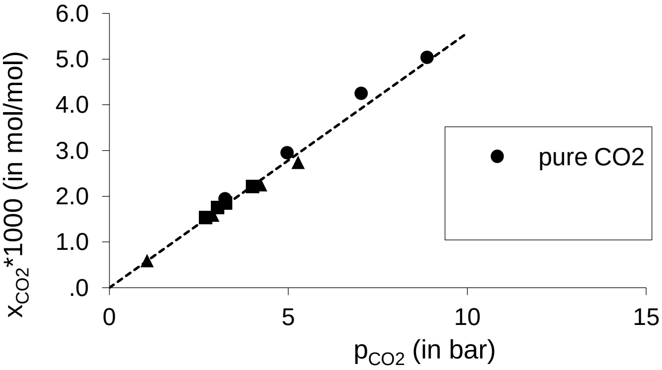

Figure 2 CO_2 solubilities in water as pure gas solubilities and as mixed gas solubilities vs. partial pressure in the gas phase

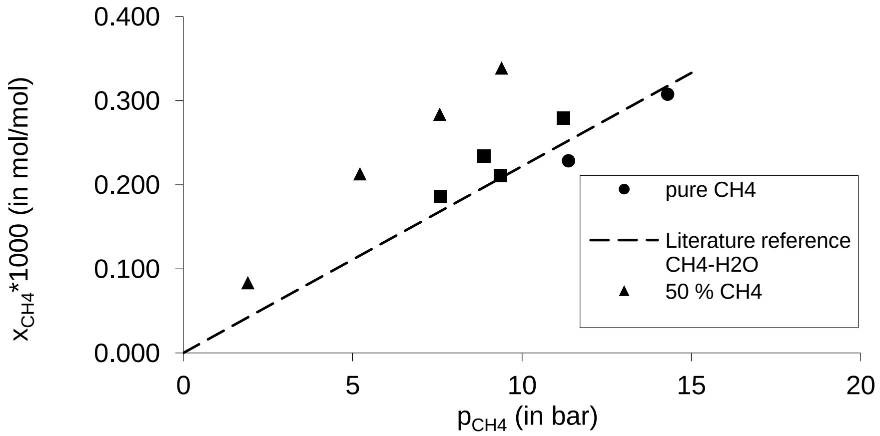

Figure 3 CH_4 solubilities in water as pure gas solubilities and as mixed gas solubilities vs. partial pressure in the gas phase

3.2 Water VLE

The evaporation of water has to be considered since a small amount of vapour is present in the gas phase. The vapour-liquid equilibrium is considered to be ideal, since the vapour pressure of water is fairly low. Therefore, the water partial pressure in the gas phase equals the vapour pressure and the ideal Raoult's law can be applied. The liquid phase is considered to consist of only water.

$$p_{H_2O} = p_{H_2O}^0(298.15\ K) \cdot x_{H_2O} \qquad (8)$$

3.3 Henry coefficients

Henry's coefficients are derived using Eq. 7. The slope of the regression line in a plot of $\ln {}^{f_i}/_{x_i}$ vs. $p - p_{H_2O}$ gives the Henry coefficient (Table 3).

Table 3: Henry coefficients for the respective gases

		Pure gas (literature)	Pure gas (own exp.)	50 % CO_2 (own exp.)	40 % CO_2 (own exp.)
CO_2-water	bar	1.624 (Carroll et al., 1991)	1.608	1.648	1.554
CH_4-water	bar	39.200 (Rettich et al, 1981)	31.530	24.835	52.569

4. Conclusion and Outlook

A novel apparatus for the determination of the solubility of mixed gases in liquids has been designed and built. Reference measurements on the systems CO_2-H_2O and CH_4-H_2O have been carried out in order to confirm the accuracy of the test cell. Solubility measurements in water with mixed gases consisting of CO_2 and CH_4 in various compositions have been made in order to quantify the influence of the dissolved species on the solubility. It has been found that dissolved carbon dioxide does influence the solubility of methane in pure, distilled water. The more CO_2 is dissolved, the greater the solubility of methane. This effect is not very pronounced in pure water but a clear trend is obvious. The influence of the dissolved CO_2 and the dissociated bicarbonate ions is greater on the methane solubility than on the solubility of CO_2. Since CO_2 is more soluble in water than methane, the effect on methane is more pronounced than the effect on CO_2. The CO_2-CH_4-water system has been tested thoroughly but more measurements with various compositional variations must be done. Also, the influence of the solute pH has to be identified since the dissociation reaction of CO_2 in water is strongly dependent on the acidity. The pH has to be measured and a rigorous model must be implemented incorporating the salting-out-effect on the methane solubility. This data can then be used to design an optimal absorption process that accounts for the increase in methane solubility when CO_2 is dissolved in water.

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