



# An automated colorimetric inline titration of CO<sub>2</sub> concentrations in solvent flow streams using a Teflon AF-2400 tube-in-tube device



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## ABSTRACT

Using a number of open source software components (Python, SciPy, OpenCV, PySerial), together with an inexpensive webcam device, an automated inline colorimetric titration methodology was developed to measure CO<sub>2</sub> concentration levels in organic flow streams emerging from a Teflon AF-2400 tube-in-tube device. A bisection search algorithm was used in combination with a curve-fitting approach to determine colorimetric titration endpoints. The results obtained are consistent with a simple 'negative exponential' model of permeation/dissolution.

## 1. Introduction

Carbon dioxide is the principle carbon-containing by-product from fossil fuel combustion. It is also released in significant quantities as a result of other industrial processes, including the production of cements from limestone. According to a recent 2016 report [1], the gas is currently being released into the atmosphere at a rate of approximately 36.2 billion tonnes per annum. Despite growing momentum towards alternative energy sources (nuclear, solar, wind, hydroelectric etc.), as of 2014 fossil fuels still accounted for around 81% of all energy production worldwide [2]. As CO<sub>2</sub> has been implicated as a major causative factor in anthropogenic post-industrial climate change, its generation and release continues to pose a significant environmental threat [3].

In addition to the increased adoption of low carbon energy sources, carbon-capture-and-storage (CCS) [4] and carbon dioxide utilisation (CDU also known as carbon capture and utilisation – CCU) [5–7] have been identified as potential strategies for the mitigation of industrial carbon dioxide release. As CO<sub>2</sub> has value as a C-1 building block in the chemical synthesis of a number of useful materials [8–15], CDU represents an attractive approach that offers both environmental and economic benefits.

Although CO<sub>2</sub> undergoes many reactions in the gas-phase, for the majority of reactions with liquid or solid reaction partners it will be

necessary to use a solvent. Indeed, it is generally the case in chemical synthesis that solvent plays a significant role in determining the outcome and/or efficiency of the desired transformation [16]. In order to obtain optimal reaction stoichiometries and kinetic parameters for any particular solvent, it will clearly be important to gain control over the concentration of CO<sub>2</sub> in that solvent.

We have previously shown [17] that continuous flow gas-liquid reactors based on the semi-permeable Teflon AF-2400 [18–20] fluoropolymer facilitate the efficient, reliable and controllable generation of homogenous flow streams of reactive gasses in organic solvents. In addition to providing a high degree of control over gas concentration levels, continuous flow approaches to organic synthesis readily lend themselves to the idea of direct utilisation of carbon dioxide at the point of production, as the gas is being generated.

Whilst remaining impermeable to the liquid phase, Teflon AF-2400 allows gasses to rapidly permeate through its amorphous microporous structure [21,22]. Initially used in synthetic applications with ozone [23], these devices have since been used with a diverse array of gasses including hydrogen [24,25], ammonia [26–28], oxygen [29–34], ethene [35–37], carbon monoxide [38,39], syngas [40] and diazomethane [41,42]. Jensen and O'Neal have also used this material to remove an ethene by-product in a continuous flow application [43]. Importantly, in the context of this present work we, and others, have demonstrated their use with carbon dioxide as a gaseous reaction

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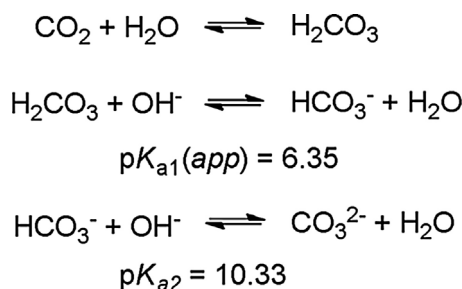
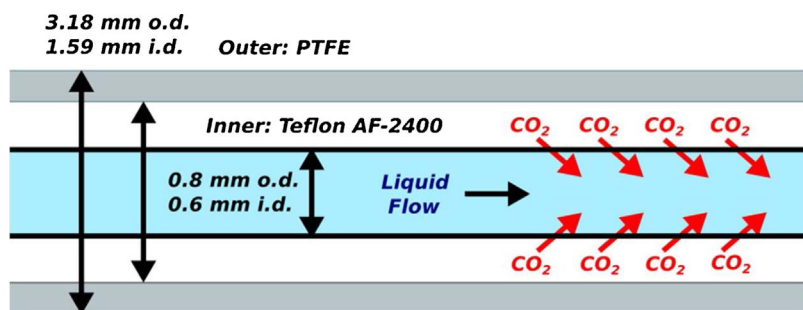


Fig. 2. Relevant equilibria in the acid-base reactivity of aqueous CO<sub>2</sub>.

partner [44,45]. Additionally, Teflon AF-2400 has been used in a number CO<sub>2</sub> sensing applications, particularly in the context of environmental research [46–48].

In applications where pressurised gas is required to achieve the desired solution concentration, the simple ‘tube-in-tube’ configuration allows an inner Teflon AF-2400 tube to be surrounded by a relatively thin jacket of pressurised gas contained in a non-permeable outer tube (Fig. 1, which shows the diameters of the tube-in-tube device used in this work). This requires only a small volume of gas to be pressurised at any time, thus minimising any hazard in the event of a rupture.

These devices potentially offer certain advantages over mechanical approaches to continuous flow gas-liquid contacting. In systems where gas and liquid flow streams meet at a mixing junction and form a biphasic outlet stream, control over the interfacial surface area, which depends on the exact morphology of the mixing junction, is by no means trivial and a number of interesting engineering approaches to this problem have been developed [49–51]. By providing an alternative mechanism for gas-liquid contact, membrane devices directly generate homogeneous flow streams of gas in liquid, circumventing many of these issues.

Jensen and Yang have performed detailed computational studies on the membrane permeation in these tube-in-tube devices which predict relatively straightforward behaviour following standard permeation-diffusion models [52]. This is in line with our previous findings using hydrogen in dichloromethane [24], where very rapid saturation was obtained (within a few seconds) and where saturation concentrations were proportional to pressure, in accordance with Henry’s law [53].

We have utilised a number of methods for the determination of gas concentrations in solutions generated using these tube-in-tube devices. In the hydrogen study mentioned above we developed a novel ‘bubble counting’ technique to quantify the out-gassing of dissolved hydrogen downstream of the back-pressure regulator. This gave results which were in agreement with standard burette measurements of out-gassing. A burette was also used to measure the out-gassing of dissolved oxygen [30]. With carbon monoxide, in-line FTIR analysis provided a convenient method of gas quantification [39]. For ammonia, its basic reactivity was utilised in an in-line colorimetric acid-base titration [26]. Very recently, Jensen and co-workers have reported an efficient automated approach, using mass flow metering, for the determination of gas take-up by solvents in tube-in-tube devices [54].

Fig. 1. Basic schematic of the Tube-in-Tube device. The liquid flowing through the inner Teflon AF-2400 tubing is represented by the blue colour. The device used in this work had a length of 10 cm (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this manuscript we report the development of an automated in-line colorimetric titration of CO<sub>2</sub> concentrations in acetonitrile flow streams generated using a Teflon AF-2400 tube-in-tube device. Incorporating a number of open-source software components (OpenCV [55,56], Python [57], SciPy [58,59], PySerial [60]) in combination with an inexpensive webcam device, the methodology described builds on our previous research in this area [61–66] and uses a computer-vision approach [67] to determine the colorimetric endpoint.

Due to the acidity of CO<sub>2</sub>, concentrations of the gas can be determined using a colorimetric titration against a known concentration of a basic species. For this work, an aqueous sodium hydroxide solution was used in conjunction with a phenolphthalein indicator (which exists in an intensely coloured purple dianionic form at pH values above about 8.2 [68]).

In the titration reaction, one equivalent of hydroxide reacts with aqueous CO<sub>2</sub> (which exists in equilibrium with the hydrated carbonic acid form H<sub>2</sub>CO<sub>3</sub>) to form the bicarbonate anion HCO<sub>3</sub><sup>−</sup>. Excess hydroxide deprotonates the bicarbonate anion to form carbonate, CO<sub>3</sub><sup>2−</sup>. The apparent pK<sub>a1</sub> value for carbonic acid [68–70], which combines the equilibrium constant for the (H<sub>2</sub>O + CO<sub>2</sub>)/H<sub>2</sub>CO<sub>3</sub> reaction with the acid dissociation constant for H<sub>2</sub>CO<sub>3</sub> is 6.35 (Fig. 2).

The pK<sub>a</sub> value for bicarbonate, HCO<sub>3</sub><sup>−</sup>, is 10.33. As such, the lower pH value for the visibility range of phenolphthalein, 8.2, will be close to the point of maximum gradient in the intermediate region of the titration curve, making it an excellent indicator for this purpose. This is illustrated in Fig. 3.

## 2. Results and discussion

The general setup for the apparatus is shown in Fig. 4. Acetonitrile is pumped from a reservoir through a tube-in-tube device with an inner 10 cm length of Teflon AF-2400 (corresponding to a fixed volume of

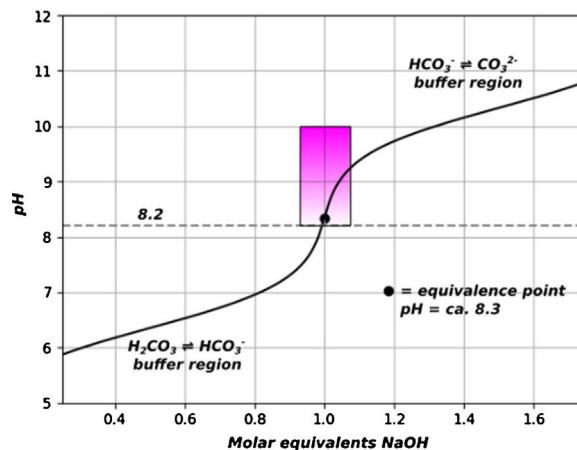


Fig. 3. The lower pH visibility limit of phenolphthalein colouration (purple box) superimposed on a calculated titration curve for aqueous CO<sub>2</sub>, showing the overlap with the equivalence point. The titration curve was calculated using pHcalc [72], a Python library for the systematic calculation of solution pH values [73].

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