

ABSORPTION OF CO₂ INTO PERFLUORINATED GAS CARRIER IN THE TAYLOR GAS–LIQUID FLOW IN A MICROCHANNEL SYSTEM

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The aim of this study was to determine the solubility of CO₂ in perfluorodecalin (PFD) which is frequently used as efficient liquid carrier of respiratory gases in bioprocess engineering. The application of perfluorinated liquid in a microsystem has been presented. Gas-liquid mass transfer during Taylor (slug) flow in a microchannel of circular cross section 0.4 mm in diameter has been investigated. A physicochemical system of the absorption of CO₂ from the CO₂/N₂ mixture in perfluorodecalin has been applied. The Henry's law constants have been found according to two theoretical approaches: physical ($H = 1.22 \cdot 10^{-3} \text{ mol/m}^3\text{Pa}$) or chemical ($H = 1.26 \cdot 10^{-3} \text{ mol/m}^3\text{Pa}$) absorption. We are hypothesising that the gas-liquid microchannel system is applicable to determine the solubility of respiratory gases in perfluorinated liquids.

Keywords: perfluorodecalin (PFD), liquid gas carrier, solubility, Taylor flow, microreactor

1. INTRODUCTION

Liquid perfluorochemicals (perfluorocarbons, PFCs) are characterised by a high solubility of respiratory gases (O₂ and CO₂) and other non-polar gases. They have raised much interest as fully safe synthetic liquid gas carriers in bioprocess and medical applications (Lowe, 2001; Pilarek and Szewczyk, 2008; Riess, 2006) confirmed by many laboratory studies and clinical investigations. It is assumed that the gas transfer rate in PFCs increases linearly with the partial pressure of a component in the gaseous phase (according to the Henry's Law) in contrast with sigmoid dissociation curves for biological gas carriers (e.g. haemoglobin or myoglobin) (Krafft and Riess, 1998; Lowe, 2002; Riess, 2001). PFCs are immiscible in aqueous and most other media and they create a separate perfluorinated phase at the bottom of the two-phase (water/PFC) systems due to their relatively high density (about 1.9 kg dm⁻³) (Lowe, 2002; Riess, 2001). In connection to their various applications it is also important that PFCs added to a reaction or culture system do not change the concentration of its components. Liquid perfluorinated gas carriers are also stable and inert compounds with high resistance to heat sterilisation (e.g. by autoclaving) and possibility for long time-storage at room temperature (Lowe, 2002; Pilarek et al., 2011a).

Bioprocess applications of liquid PFCs are mainly related to supplying them into culture systems as gas carriers (mainly O₂) as well as scavengers of gaseous by-products (mainly CO₂) of cellular metabolism. Many studies have shown that the application of gas saturated perfluorinated liquids can improve efficiency of microbial (Elibol and Mavituna, 1997; Pilarek and Szewczyk, 2008; Pilarek et al., 2011a), plant cell (Pilarek and Szewczyk, 2008) and animal cell cultures (Shiba *et al.*, 1998; Rappaport, 2003; Pilarek *et al.*, 2011b) and thus lead to improved growth or metabolite biosynthesis in cultures of various

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kinds of cells. Generally, applications of PFCs are still limited due to their relatively high cost, which makes their use in large-scale bioprocesses uneconomical. However, PFCs could successfully be used in miniature-scale processes and in microbioreactor cultivations of various kinds of cells to prevent oxygen or carbon dioxide limitation during grow to high cell densities, especially in high throughput screening approaches (Pilarek et al., 2011a; Ukkonen et al., 2011). In view of the unusual mechanism of dissolution of gases in perfluorinated liquid, it would be interesting to determine the nature of the absorption process and the values of CO₂ solubility into perfluorodecalin (PFD).

A typical apparatus for this type of investigations is the laminar-jet setup (Pohorecki and Moniuk, 1988). However, because of the cost of fluorinated liquids, using such equipment is uneconomical and problematic. We hypothesise that an application of a gas-liquid microreactor system could be more feasible. Mass transfer and hydrodynamics of the Taylor flow in microchannels have widely been investigated (Qian and Lawal, 2006; Sobieszuk et al., 2010; Eskin and Mostowfi, 2012; Sobieszuk et al., 2012). There are lot of experimental data on volumetric mass transfer coefficient ($k_L a$) values in the Taylor flow (Kashid et al., 2011; Sobieszuk et al., 2008; Yue et al., 2007) and k_L (Sobieszuk et al., 2011) values. Therefore, a series of experiments involving the study on the rate of CO₂ absorption into perfluorodecalin (PFD) were done. On this basis and using the available correlations for mass transfer in the Taylor flow, the values of the Henry's law constant have been determined. The aim of this study was to determine the solubility of CO₂ into perfluorodecalin which is frequently used as an efficient liquid carrier of respiratory gases in bioprocess engineering. To the best of our knowledge this is the first attempt to apply a microreactor system to defining the mechanism of gas absorption in liquid PFC and also the first report of the application of perfluorinated gas carrier in microchannel system in general.

2. EXPERIMENTAL SYSTEM

A glass, Y-shaped microreactor, with inlet channels 120° apart from each other and from the main channel has been used. The cross-section of all the channels was circular with 0.4 mm diameter. The main microchannel length was 100 mm. The experimental set-up is shown in Fig. 1.

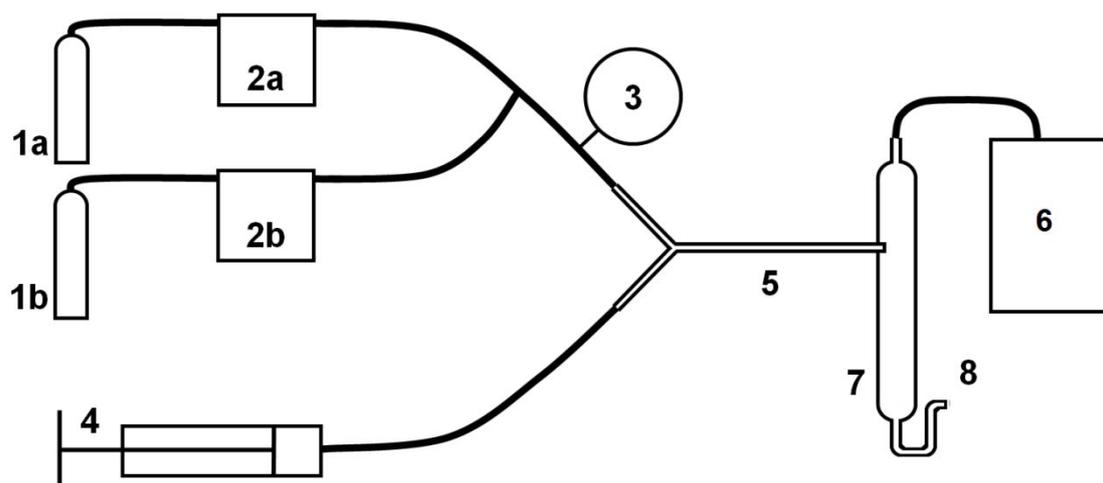


Fig. 1. Experimental set-up,

1a, 1b – gas bottles with CO₂ and N₂; 2a, 2b – gas flow regulators; 3 – manometer; 4 - syringe pump;
5 – Y-shaped microreactor; 6 – gas chromatograph ; 7 – separator; 8 - liquid outlet

A physicochemical system of the absorption of CO₂ from the CO₂/N₂ mixture into a pure PFD has been applied. The gases (N₂ and CO₂) were supplied from cylinders through reducing valves and gas flow

regulators. Both gases were mixed before the inlet to the microchannel, and pressure was measured. PFD (cis/trans C₁₀F₁₈; ABCR GmbH, Germany) was supplied by a syringe pump. The liquid flow was measured using a measuring cylinder and a stop watch. The two-phase mixture leaving the microchannel was separated in a separator. The gas was directed to the gas chromatograph (Shimadzu GC 2014). The rate of absorption was measured twice: once for the entire microreactor (Fig. 2a), and for the second time using only the phase contactor and the separator, without the main gas – liquid microchannel (Fig. 2b) in order to eliminate the end effects for each experiment conditions. The properties of PFD (density, viscosity, surface tension) were used based on data presented by Pilarek et al. (2006). The diffusivity of CO₂ in perfluorodecalin was calculated based on the Wilke and Chang method. All experiments were conducted at the room temperature. Three concentrations of CO₂ at the gas inlet were used: 30 %, 50 % and 70 %, respectively. For each experimental series the gas flow was kept constant and equalled $3.33 \cdot 10^{-8}$ m³/s. The flow ranges of pure PFD were from $1.2 \cdot 10^{-8}$ to $3.1 \cdot 10^{-8}$ m³/s. The CO₂ absorption rate was calculated from the gas concentration difference between the inlet and the outlet from microreactor.

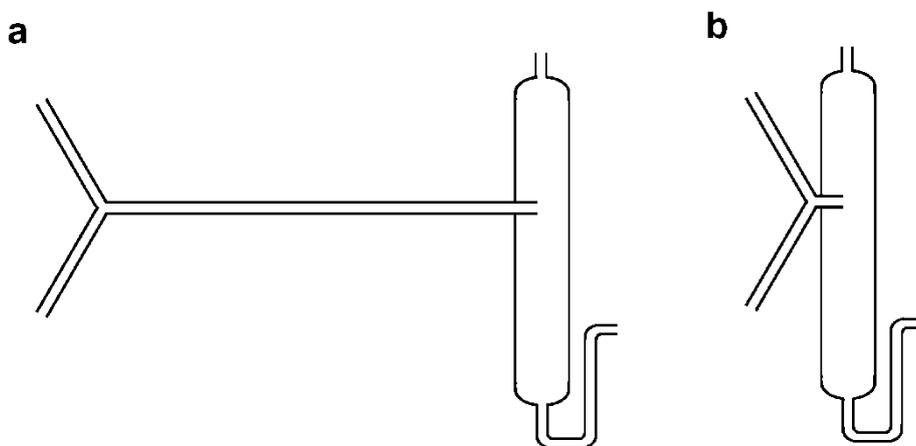


Fig. 2. Microchannel set up used in experiments: a) microreactor – separator, b) phase contactor – separator

3. RESULTS AND DISCUSSION

The values of CO₂ concentration in CO₂/N₂ mixture at the outlet of both studied microchannel devices have been presented in Fig 3. The significant differences in concentration have been noted for all the studied cases. These results allow to determine the absorption rate only in the microchannel. However, our method could not be effective in the case of gases characterised by lower solubility in PFCs (e.g. O₂ or CO) since it could be observed that too large a part of PFC is absorbed in the phase separator. Due to this fact the differences between the measured concentrations of the absorbed gas at the inlet of the microreactor – separator system and the contactor – separator system might be too low in order to ensure sufficiently accurate values of the absorption rate.

The absorption rate in microchannel as a function of the superficial velocity of the two-phase flow has been shown in Fig. 4. An expected upward trend of the absorption rate with an increasing two-phase flow velocity (i.e. higher values of the mass transfer coefficient at higher values of two-phase flow velocity) as well as with the increasing CO₂ concentration at the gas inlet (i.e. with increased driving force of the absorption process) has been observed.

The Henry's law constant can be determined for the studied CO₂ – PFD system based on the estimated values of the CO₂ absorption rates in the applied microchannel device. The mechanism of gas dissolution in perfluorinated liquids quoted in the literature (Deschamps et al., 2007) does not explicitly define whether it is chemical or physical absorption. Therefore, two approaches have been attempted for further discussion.

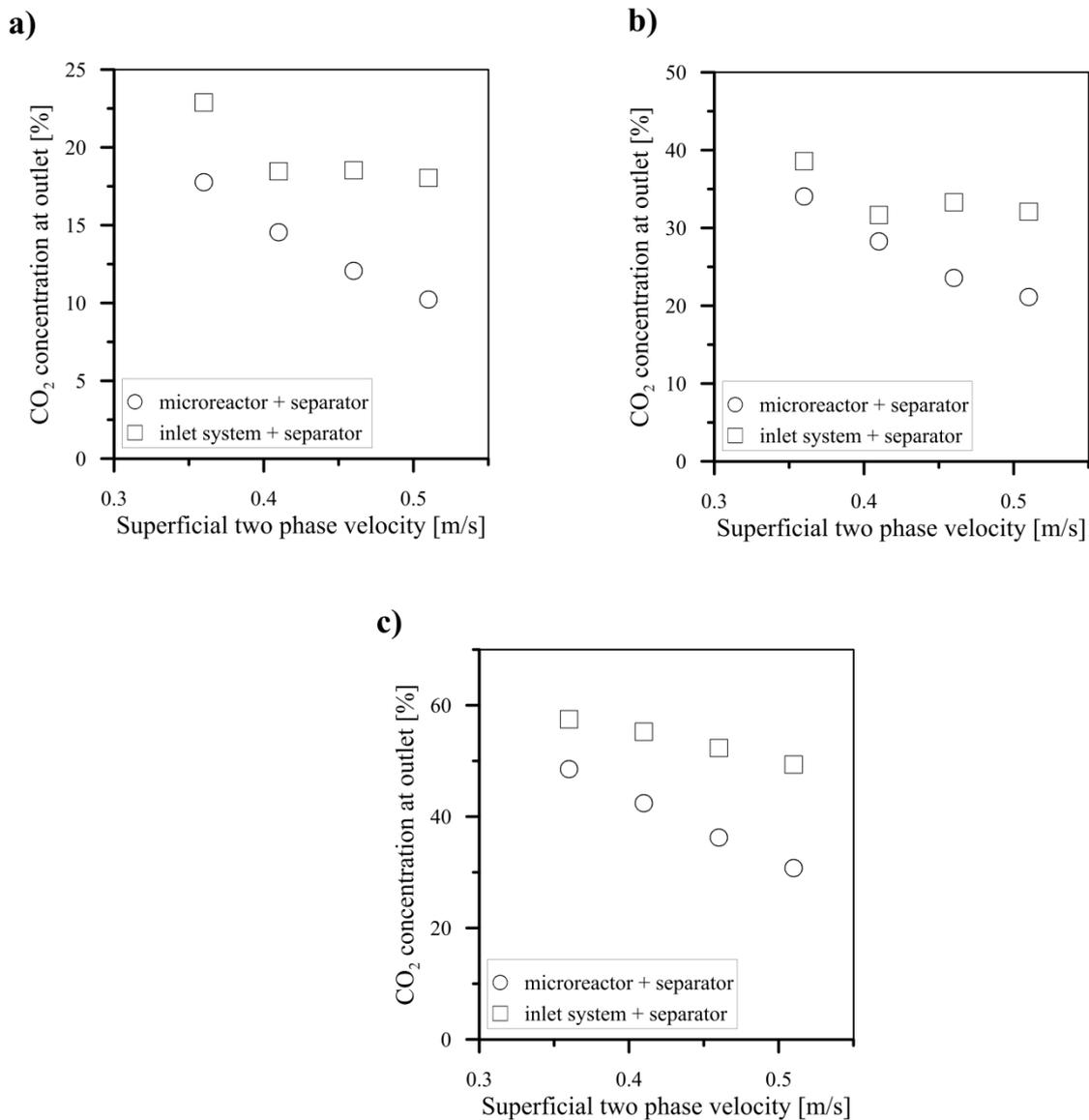


Fig. 3. Concentration of CO₂ in CO₂/N₂ mixture at outlet in microreactor-separator system and inlet – separator system in the case of various CO₂ concentrations at the inlet: a) 30%, b) 50% and c) 70%

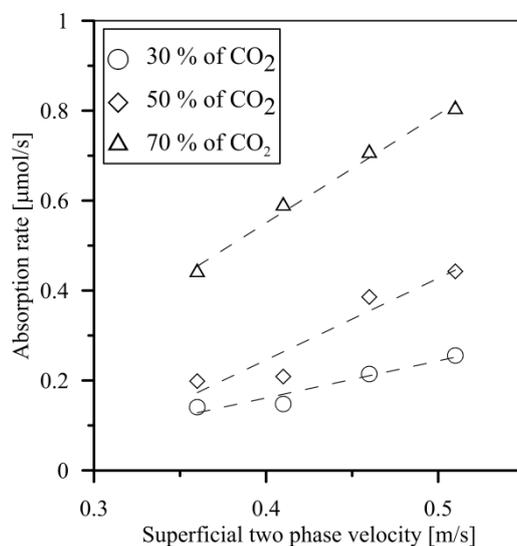


Fig. 4. CO₂ absorption rate in microchannel as a function of the superficial two-phase flow velocity

As it is commonly known, the absorption rate is defined as follows

$$N = k_L a V \Delta c \quad (1)$$

The values of the volumetric mass transfer coefficient for the various gas/liquid systems are available in the literature. Sobieszuk et al. (2011) proposed the correlation for k_L calculation in the gas-liquid microchannel system. However, in the case of our present study involving a heterogeneous microsystem the interfacial area remains unknown, so the correlation due to Yue et al. (2007) has been used. They proposed the following correlation for the volumetric mass transfer coefficient:

$$Sh \cdot a \cdot d = 0.084 Re_G^{0.213} Re_L^{0.937} Sc_L^{0.5} \quad (2)$$

The driving force of the process is given by

$$\Delta c = \frac{(c_{i1} - c_1) - (c_{i2} - c_2)}{\ln \frac{c_{i1} - c_1}{c_{i2} - c_2}} \quad (3)$$

The Henry's law constant is defined as

$$c = H \cdot p \quad (4)$$

Since the inlet concentration of CO₂ in the liquid phase (PFD) is 0 ($c_1 = 0$) and the gas-side mass transfer resistance can be neglected, Eq. (3) simplifies to

$$\Delta c = \frac{H p_1 - (H p_2 - c_2)}{\ln \frac{H p_1}{H p_2 - c_2}} \quad (5)$$

For physical absorption the outlet concentration of CO₂ in the liquid phase can be calculated based on mass balance

$$c_2 = \frac{Q_{G1} \frac{p_1}{RT} - Q_{G2} \frac{p_2}{RT}}{Q_L} \quad (6)$$

After rearranging Equations (1), (3) and (5), the absorption rate can be expressed as follows

$$N = k_L a V \frac{H p_1 - \left(H p_2 - \frac{Q_{G1} \frac{p_1}{RT} - Q_{G2} \frac{p_2}{RT}}{Q_L} \right)}{\ln \frac{H p_1}{H p_2 - \frac{Q_{G1} \frac{p_1}{RT} - Q_{G2} \frac{p_2}{RT}}{Q_L}}} \quad (7)$$

In case of chemical absorption it can be assumed that the outlet concentration of CO₂ in the liquid phase is 0 ($c_2=0$). Hence

$$\Delta c = \frac{p_1 - p_2}{\ln \frac{p_1}{p_2}} H \quad (8)$$

and finally the absorption rate is described by a simple equation

$$N = k_L a V \frac{p_1 - p_2}{\ln \frac{p_1}{p_2}} H \quad (9)$$

Based on the experimental data of the absorption rate of CO₂ into PFD for different values of the two-phase superficial flow velocity the Henry's law constant could be determined. In case of physical absorption the values of H were calculated from Eq. (7) and the average value has been obtained as $H = 1.22 \cdot 10^{-3}$ mol/m³Pa with standard deviation of $3.14 \cdot 10^{-4}$ mol/m³Pa. The results estimated for chemical absorption of CO₂ into PFD defined by Eq. (9) are shown in Fig. 5.

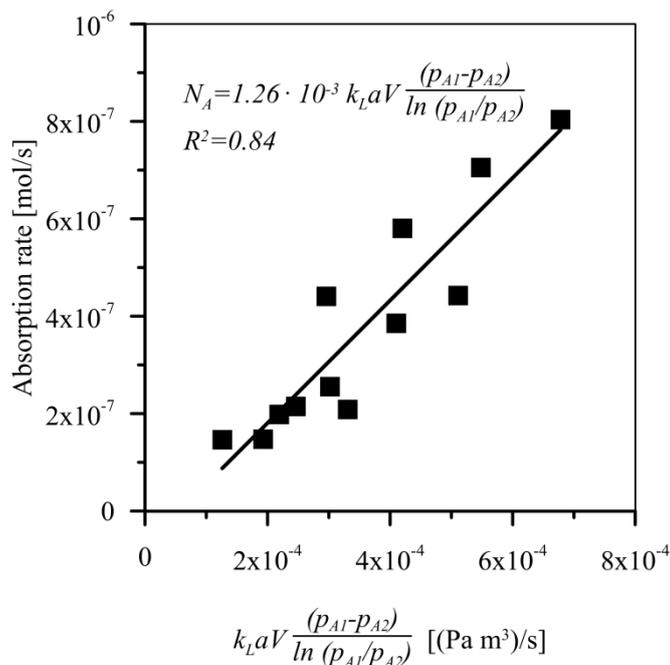


Fig. 5. Determination of the Henry's law constant for chemical absorption based on Eq. (9)

As can be seen $H = 1.26 \cdot 10^{-3}$ mol/m³Pa with the correlation coefficient $R^2 = 0.84$. It should be emphasised that the obtained values are very close to each other, but are subject to an experimental error. Such errors resulted from the effects of short microchannel used and from relatively low CO₂ solubility in PFD.

4. CONCLUSIONS

The rates of CO₂ absorption in PFD in the Taylor flow in microchannel have been estimated. The Henry's law constants have been found for the studied microsystem based on two theoretical approaches, physical or chemical absorption processes. Both obtained values of H are very close to each other and are in accordance with previously published literature data of CO₂ solubility in PFD (Deschamps et al., 2007; Pilarek and Szewczyk, 2008). Nevertheless, we conclude that the mechanism (physical or chemical) of CO₂ absorption in PFD cannot be explicitly defined based on the results of our experiments. It turned out that the applied 100 mm long microchannel was too short to observe any differences between the two examined kinds of absorption. Using microdevices with a longer microchannel enabling greater residence time of media could provide more accurate experimental data.

Finally, we can state that the gas-liquid microchannel system is applicable for experimental determination of respiratory gases solubility in perfluorinated liquids.

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SYMBOLS

a	specific interfacial area, m ⁻¹
c	concentration of CO ₂ in liquid phase, kmol·m ⁻³
D	diffusivity of CO ₂ into perfluorodecalin, m ² ·s ⁻¹
d	microchannel diameter, m
H	Henry's law constant, mol·m ⁻³ ·Pa ⁻¹
k_L	liquid side mass transfer coefficient, m·s ⁻¹
N	absorption rate, mol·s ⁻¹
p	partial pressure, Pa
Q	flow rate, m ³ ·s ⁻¹
R	gas constant, J·mol ⁻¹ ·K ⁻¹
$Re_G = u_G \cdot d \cdot \rho_G / \mu_G$	Reynolds number for gas phase
$Re_L = u_L \cdot d \cdot \rho_L / \mu_L$	Reynolds number for liquid phase
$Sc_L = \mu_L / (\rho_L \cdot D)$	Schmidt number for liquid phase
$Sh = k_L \cdot d / D$	Sherwood number
T	temperature, K
u	superficial velocity, m·s ⁻¹
V	microchannel volume, m ³

Greek symbols

ρ	density, kg·m ⁻³
μ	viscosity, Pa·s
σ	surface tension, N·m ⁻¹

Subscripts

1	inlet
2	outlet
i	interfacial area
G	gas
L	liquid

Abbreviations

PFC	perfluorochemical
PFD	perfluorodecalin

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