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Solubility and diffusivity of carbon dioxide in perfluoropolyethers

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ABSTRACT

The main objective of this work was to obtain new data for equilibrium and transport properties in the absorption of carbon dioxide into liquid solvents not yet investigated to this purpose. To this end, an experimental setup for measuring gas solubility and diffusivity in non-volatile solvents was designed, realized, and tested by comparison with literature data for the methane/*n*-dodecane pair.

The solubility of carbon dioxide, nitrogen and oxygen in two different perfluoropolyethers, Fomblin® M03 and Fomblin® Y04, was measured at different temperature ranging from 10 °C to 100 °C and for pressures up to 7 bar. The diffusivity of carbon dioxide in the solvents was measured at 25 °C and 50 °C, through a pressure decay method.

The results obtained in terms of carbon dioxide solubility and selectivity over other gases are encouraging for the possible use of Fomblin® perfluoropolyethers for the absorption of carbon dioxide from flue gases of industrial plants, also due to the complete immiscibility with water of this solvents. New compounds with similar chemical structure are being developed and tested in order to maximize the performances of the absorption process.

1. Introduction

The physical absorption of acid gases by organic solvents is becoming more and more interesting thanks to the growing attention given to the capture and storage of CO_2 in power plants. With respect to alternative separation technologies such as membrane processes or pressure swing adsorption, which require a high pressure feed, physical absorption is particularly suitable for CO_2 removal from syngas or flue gas, since it can be performed at near-atmospheric pressure, while the desorption step is accomplished by increasing the temperature and/or applying vacuum. Moreover, compared with chemical absorption (mainly in amines), physical absorption requires a largely lower regeneration energy (Aschenbrenner and Styring, 2011).

The main properties a good solvent should show are low volatility, high thermal and chemical stability, high absorbed gas solubility and selectivity with respect to other gas, non-toxicity, and low viscosity. In addition to several solvents studied by authors such as Aschenbrenner and Styring (2011), including glycerol, glycerol carbonate, and various polyethylene glycols, perfluoropolyethers (PFPEs) can be taken into consideration, due to their excellent thermal and chemical resistance, their non-flammability, and non-toxicity. An important advantage of this class of solvents is that, unlike glycols, they are completely immiscible with water, and thus do not absorb the large amount of water present in flue gases.

In this work we measured, at different temperatures and pressures, the solubility of CO_2, N_2 and O_2 and the diffusivity

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Table 1 – Main physical properties of the used solvents.

Solvent	n-C_{12}	Fomblin® M03	Fomblin® Y04
Supplier	Sigma–Aldrich	Solvay	Solvay
Average molecular weight (g/mol)	173.33	3900	2000
Density @ 20 °C (kg/L)	0.75	1.81	1.87
Kinematic viscosity @ 20 °C (cSt)	1.8	30	38
Flash point (°C)	71	Non-flammable	Non-flammable
Vapor pressure (mbar)[a]			
@ 20 °C	0.12	8.80×10^{-5}	0.069
@ 40 °C	–	1.27×10^{-4}	0.220
@ 50 °C	1.18	–	–
@ 70 °C	–	2.20×10^{-4}	0.972
@ 100 °C	–	2.99×10^{-4}	3.383

[a] The vapor pressure values for the three solvents are indicated at temperatures near those used for solubility measurement. For n-dodecane, the values are calculated by using the correlation given by Perry and Green (1997) in Tables 2–6. For Fomblin M03 and Y04, the values at 20 °C and 40 °C are measured by the supplier; these data are then used to find the parameters (A and B) of a simple correlation of the form: $\log_{10}(P) = A - B/T$ (Perry and Green, 1997, Eq. (4-151)). The vapor pressure values at 70 °C and 100 °C are then extrapolated using that correlation.

of CO_2 in different PFPEs, aiming to evaluate the possibility to use them as solvents in CO_2 physical absorption processes.

The methodology and the experimental setup used were preliminarily verified by comparison with literature data, using the methane/n-dodecane solute/solvent pair.

2. Materials and methods

2.1. Materials

Normal dodecane, with purity over 99%, was supplied by Sigma–Aldrich.

Two PFPEs (Fomblin® M03, Fomblin® Y04), having different chemical structure and a purity over 99%, were supplied by Solvay Specialty Polymers:

- Fomblin® M03, linear: CF_3-[$(OCF_2CF_2)_m$-$(OCF_2)_n$]-O-CF_3 with $m/n \approx 1$;
- Fomblin® Y04, branched: CF_3-[$(OCF(CF_3)CF_2)_m$-$(OCF_2)_n$]-O-CF_3 with $m/n \gg 40$.

The main physical properties of these solvents, as reported in the supplier datasheet, are presented in Table 1.

The gases (N_2, O_2, CO_2, CH_4) were all supplied by SIAD and were of analytical grade (purity ≥99,999%).

2.2. Experimental setup

The P&ID of the experimental setup, used for measuring the solubility and diffusivity of gases in non-volatile liquids, is shown in Fig. 1. The setup main components are two stainless steel tanks. The first one (D1) is connected through the valve V1 to a compressed gas cylinder equipped with a pressure reducer, and to the second tank (D2) through the valve V2. Both tanks are connected to the vacuum pump G1 through the valve V3. Upstream the vacuum pump, a liquid-nitrogen-cooled cold trap is placed, in order to avoid both the contamination of D1 and D2 via the retro-diffusion of pump oil vapor and the contamination of the pump oil by the vapor of the solvent in D2. D2 can be filled with liquids through a filling tube and the valve V4; the liquid can be discharged from the bottom of the tank through V5. The liquid in D2 is stirred by a PTFE coated stir bar using a magnetic stirrer (not depicted) on which D2 is placed.

D1 is equipped with a thermocouple (TE10) and a pressure transducer (PT20) with measuring range 1–26 bar; D2 is equipped with a thermocouple (TE11) and two pressure transducers (PT21 and PT22) with different full scales, covering the range 0–6 bar. The measured data are acquired by a datalogger and stored on a PC.

D2 is placed into a larger insulated open-top tank, inside which an ethylene glycol aqueous solution from a cooling/heating bath is circulated, in order to control precisely the test temperature in D2.

The main specifications of the components of the setup are listed in Table 2. Bellows sealed valves with really low allowable leakage rate are used to isolate the absorption cell D2, in order to maximize the precision of pressure measurements; elsewhere, ball valves are used.

Table 2 – List of equipment and instrumentation for the experimental setup.

Item	Description	Notes
D1	Gas charge cell	Total volume (connection included): 327 mL
D2	Diffusion/absorption cell	Total volume (connection included): 353 mL Equipped with PTFE-coated magnetic stir bar
D3	Open top tank	Total volume 8 L
D4	Dewar flask	Filled with liquid nitrogen
D5	Cold trap	Made of borosilicate glass
V1, V3	Ball valves	Maximum leakage rate: 0.1 cm^3/min (standard condition)
V2, V4, V5	Bellows sealed valves	Maximum leakage rate: 2.4×10^{-7} cm^3/min (standard condition)
G1	Rotary vane pump	Maximum vacuum 10^{-6} bar
TE10, TE11	Type K thermocouples	AISI 310 sheathed, 3 mm diameter
PT20	Pressure transducer	Pressure range 1–26 bar, precision 0.2% f.s. (50 mbar)
PT21	Pressure transducer	Pressure range 0–6 bar, precision 0.2% f.s. (12 mbar)
PT22	Pressure transducer	Pressure range 0–1 bar, precision 0.2% f.s. (2 mbar)
–	Cooling/heating circulating bath	Precision ±0.1 K; temperature range −25/100 °C