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A Novel Approach for Measuring Gas Solubility in Liquids Using a Tube-in-Tube Membrane Contactor

A novel approach using a semipermeable Teflon AF-2400 tube-in-tube membrane contactor was developed for the measurement of gas solubility in organic solvents. This membrane ensures gas saturation of liquids in continuous flow at a specific pressure and temperature. After liquid decompression, the amount of gas outgassed was measured with a bubble meter and used for solubility calculation. The proposed method was applied to the measurement of oxygen solubility in toluene and benzyl alcohol. Validation experiments were initially performed by comparing the obtained oxygen solubility in toluene with literature data. With higher temperature, the solubility of oxygen in benzyl alcohol was found to increase, indicating that the oxygen-dissolving process is endothermic. Finally, an empirical correlation of Henry's law constant as a function of temperature was determined.

1 Introduction

Gas solubility data in organic solvents have a high importance in chemical industry for the design of various unit operations, e.g., separators and reactors, and the solubility of oxygen is probably one of the most essential [1]. Generally, the solubility of oxygen in liquid can be experimentally measured with analytical or synthetic methods [2, 3]. These two main approaches are classified based on whether the equilibrium compositions are determined (analytically) and whether the total mixture is prepared with predetermined amounts of the components (synthetically). For example, Anthony et al. [4] measured oxygen solubility in ionic liquids using an analytical gravimetric method. The compositions were calculated according to the weight change of liquids on a gravimetric microbalance before and after gas adsorption. Lopez-Castillo et al. [5] evaluated the oxygen solubility in CO_2-expanded liquids through analyzing the samples of the vapor and liquid phases at equilibrium with a gas chromatograph. Fischer and Wilken [6] determined oxygen solubility in organic solvents by means of a static synthetic method, where the amount of pure components was precisely known and the changes of temperature and pressure during experiments were monitored.

Oxidation of alcohols is one of the most fundamental organic transformations and has great importance in chemical synthesis [7–9]. Traditionally, this type of reactions involves stoichiometric inorganic oxidants (chromium(VI) or permanganate), leading to serious environmental problems [10]. From the view of green chemistry, there is a growing demand to use molecular oxygen as oxidant for catalytic oxidation of alcohols [10–12]. The amount of available oxygen influences the extent of oxidation reactions. On one hand, local shortage of oxygen, caused by the low solubility of oxygen in solvents and poor mass transfer, could potentially limit the reaction rate [11–19]. On the other hand, an excess of oxygen might cause overoxidation of products or catalysts [11, 20–22]. Mixtures of oxygen and organic solvents under elevated temperatures and pressures could also raise serious safety issues [23]. Thus, more data on oxygen solubility under reaction pressures and temperatures are strongly required.

Recent advances in membrane science provide the opportunity to develop new methods for the measurement of oxygen solubility. Particularly, Teflon AF-2400 uniquely combines excellent chemical resistance, thermal stability, and mechanical properties with high fractional free volume [24, 25]. Its permeability characteristics to gas and liquid assure simultaneously high flux of gas and low permeation of liquid through the membrane.

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The Ley group first developed a tube-in-tube membrane contactor, which comprised an inner Teflon AF-2400 tube and an outer polytetrafluoroethylene (PTFE) tube, and applied it to various reactions like ozonolysis, hydrogenation, etc. [26–28]. Generally, liquid is pumped through the inner tube and gas is pressurized at the annulus between the inner and outer tubes. When the liquid is flowing within the inner tube, the pressurized gas can permeate through the semipermeable tube and be dissolved in the liquid until equilibrium is reached. The saturation concentration of gas in the liquid within the tube-in-tube contactor is observed to approximately obey Henry's law [19, 29]. In this study, the Teflon AF-2400 tube-in-tube membrane contactor was employed as a novel apparatus for the measurement of gas solubility in liquids, as exemplified by the case of oxygen in toluene and benzyl alcohol.

2 Experimental

2.1 Materials

The oxygen (99.995 %) used in this study was obtained from BOC. Toluene ($\geq$ 99.5 %) and benzyl alcohol ($\geq$ 99 %) were from Sigma-Aldrich. All materials were used without further purification.

2.2 Apparatus

The schematic of the tube-in-tube membrane contactor setup is illustrated in Fig. 1. The membrane contactor consists of an inner Teflon AF-2400 tube with an inner diameter (ID) of 0.8 mm and outer diameter (OD) of 1.0 mm (Biogeneral) and an outer PTFE tube with an ID of 2.4 mm and OD of 3.2 mm (Agilent). The various parts of the setup were connected with perfluoroalkoxy (PFA) tubing (ID 1.0 mm, OD 1.6 mm) unless otherwise specified. The total length of the tube-in-tube membrane contactor was 100 cm. Liquid, i.e., toluene or benzyl alcohol, was pumped through the inner tube, while oxygen flowed in the annulus between the inner and outer tubes. The liquid flow rate was controlled with an HPLC pump (Knauer, P 2.1S) and the liquid pressure was maintained by a backpressure regu-

lator (BPR; Zaiput, BPR-01). The oxygen flow was controlled with a mass flow controller (Brooks, GF40 series) and the oxygen pressure (P_{O_2}) was sustained by another backpressure regulator (Swagelok, K series). The actual pressures of gas and liquid were measured by two pressure sensors (Zaiput, Hastelloy/PFA wetted parts).

The tube-in-tube membrane contactor was submerged in a stirred oil bath. The temperature of the oil bath was controlled by a hot plate fitted with a thermocouple (Stuart, US152). Liquid was prebubbled with oxygen using a gas sparger for 0.5 h at room temperature and atmospheric pressure to remove other dissolved gases. When the oil bath temperature and oxygen pressure stabilized, the liquid was pumped into the contactor. Oxygen passed through the semipermeable membrane and dissolved into the liquid, reaching equilibrium in the contactor when the liquid residence time was long enough [19, 30]. When the liquid flowed out of the contactor and passed through the backpressure regulator, the dissolved oxygen outgassed from the liquid due to decompression. The mixture of gas and liquid was directed to a 250-mL glass vessel separator, prefluxed with pure oxygen and located in a water bath maintained at 298 K, where gas and liquid were separated. The liquid collected in the separator was thus saturated with oxygen at 1 bar pressure and 298 K.

The gas flow out from the separator included the contribution from the outgassed oxygen saturated with vapor and the gas volume change in the separator caused by the collection of liquid (see Fig. 1). It was measured with a 1-mL bubble flow meter connected to the outlet of the separator by a silicon rubber tubing ($\sim$ 3 mm ID). The bubble meter contained $\sim$ 1 mL soapy water which was assumed to be saturated with oxygen. Complete sealing of the separator was checked to avoid measurement errors caused by oxygen loss to the surroundings.

The experiment was carried out by varying the oxygen pressure from 1 to 10 bar while keeping the liquid pressure at 10 bar. All pressures in this study are absolute. The temperature of the experiment ranged from 298 K to 393 K. At a given oxygen pressure, three different liquid flow rates (0.25–0.45 mL min^{-1}) were applied and the gas flow rate from the separator was measured at least three times at each liquid flow rate.

2.3 Calculations

Liquid dissolution in the membrane and further permeation to the gas phase is neglected in the membrane contactor. In the separator, the gas phase is assumed to be saturated with organic vapor which has to be subtracted from the measured gas flow rate. However, the loss of organic solvent into the gas phase can be neglected due to its low amount, i.e., < 0.1 % of the liquid flow. Henry's law constant (H) at given temperature T is defined by:
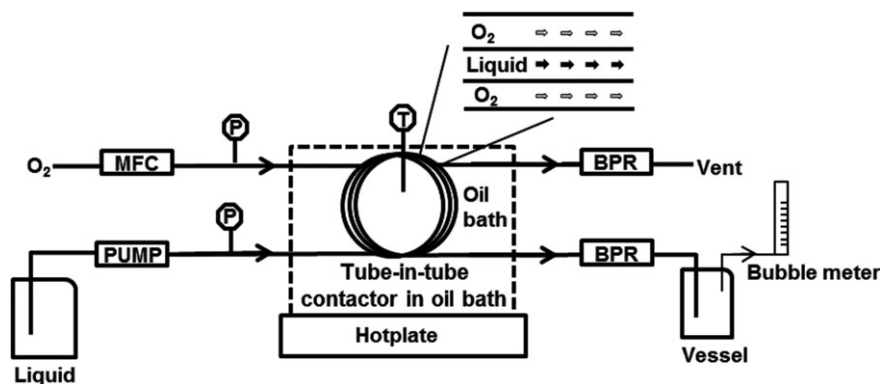

Figure 1. Schematic of the tube-in-tube membrane contactor setup used for the measurement of Henry's law constants. MFC: mass flow controller; PUMP: HPLC pump; P: pressure sensor; T: thermocouple for temperature control; BPR: backpressure regulator.

$$H = \frac{P_{O_2}}{x(T)} \tag{1}$$

where P_{O2} is the oxygen pressure and x is the mole fraction of oxygen in the liquid at given temperature T. The amount of oxygen outgassed per liquid volume (ϕ_{O2}) can be expressed as:

$$\phi_{O_2}(T) = \frac{\tilde{V}_{O_2}\rho_L}{M_L H}P_{O_2} - \frac{\tilde{V}_{O_2}\rho_L}{M_L H_{298\,K}}P_{atm} \tag{2}$$

where T is the experiment temperature, $\tilde{V}_{O2}$ is the molar volume of oxygen at STP (22400 mL mol^{-1}); ρ_L is the density of liquid (g mL^{-1}); M_L is molar mass of liquid (g mol^{-1}), P_{O2} is the oxygen pressure (bar), P_{atm} is the atmospheric pressure (1 bar), H is Henry's law constant at experiment temperature T, H_{298K} is Henry's law constant at 298 K. By plotting ϕ_{O2} vs P_{O2}, the Henry's constant at given temperature can be calculated. Detailed derivation of Eq. (2) can be found in the Supporting Information.

3 Results and Discussion

Initially, the method was validated by measuring oxygen solubility in toluene. The measurements were carried out at 298 K and 348 K with oxygen pressures up to 10 bar. The experimental data of ϕ_{O2}–P_{O2} are plotted in Fig. 2. The slopes of the fitting lines were 0.20001 mL mL$_{Liquid}$$^{-1}$bar^{-1} for 298 K and 0.21922 mL mL$_{Liquid}$$^{-1}$bar^{-1} for 348 K.

Henry's law constants were calculated to be 1057 bar and 965 bar, respectively, and compared with literature data which were obtained with static synthetic apparatuses [6, 31, 32] as depicted in Fig. 3. The values in this work are very close to literature data, and the differences at the same temperature ($\Delta H/H \times 100$ %) are within 5 %, proving the reliability of this method.

After validation of the method, oxygen solubility in benzyl alcohol was measured at temperatures from 298 K to 393 K with oxygen pressures of up to 10 bar. The experimental ϕ_{O2}–P_{O2} data are given in Fig. 4. The slopes of the fitting lines, together with the calculated Henry's law constants and the mole fraction of oxygen (x) in benzyl alcohol under 1 bar oxygen pressure, are summarized in Tab. 1. To provide oxygen solubility data, the saturation concentration of oxygen (c_{O2}) in
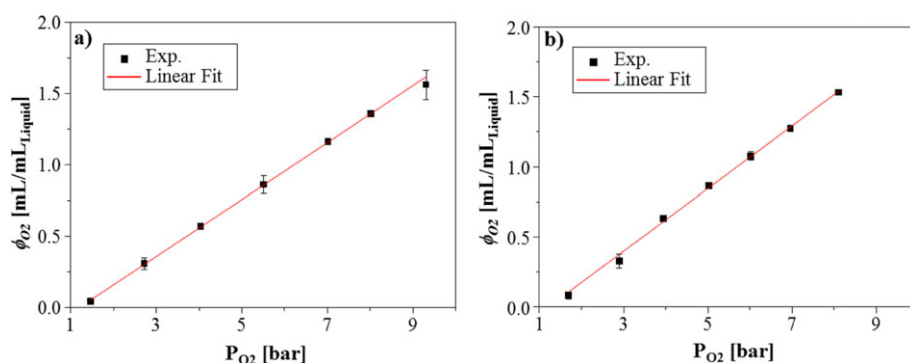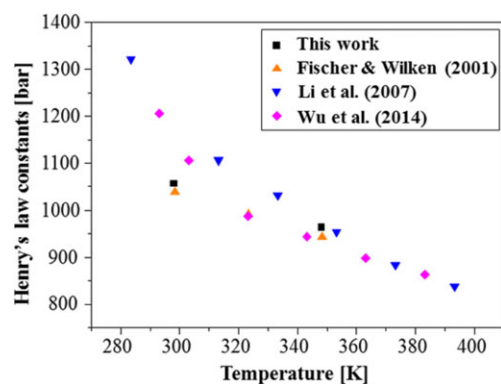

Figure 3. Comparison of Henry's law constants of oxygen in toluene found in this work with literature [6, 31, 32].

Table 1. Henry's law constants and oxygen solubilities at 1 bar in benzyl alcohol.

T [K]	Slope [mL mL$_{Liquid}$$^{-1}$bar^{-1}]	Oxygen solubility		H [bar]
		Mole fraction $x \times 10^3$	Saturation concentration c_{O2} [mM]	
298	0.06223	0.289	2.78	3462
313	0.06468	0.300	2.89	3332
333	0.06658	0.309	2.97	3237
353	0.06933	0.322	3.10	3108
373	0.07290	0.338	3.25	2956
393	0.07479	0.347	3.34	2881

benzyl alcohol under 1 bar oxygen pressure is also provided for each temperature.

As seen in Tab. 1, the solubility of oxygen in benzyl alcohol increases with temperature. This trend agrees with that of oxygen in toluene, indicating that the solubilization is endothermic [31, 32]. Henry's law constant for oxygen in benzyl alcohol at 298 K is 3462 bar, which is three times higher than that in toluene (1057 bar). This is probably caused by a lower value for oxygen-benzyl alcohol enthalpy of solvation, indicating a less favorable interaction between oxygen and benzyl alcohol than of oxygen with toluene [32].

At low pressure, Henry's law constants can be considered to be independent of pressure, and thus they can be expressed as a function of temperature [31–33]:

$$\ln(H) = \frac{a}{T} + b \tag{3}$$

where a and b are fitting parameters. The experimental data from Tab. 1 are plotted in Fig. 5 as an $\ln(H)$ vs. $1/T$ plot. A straight line is
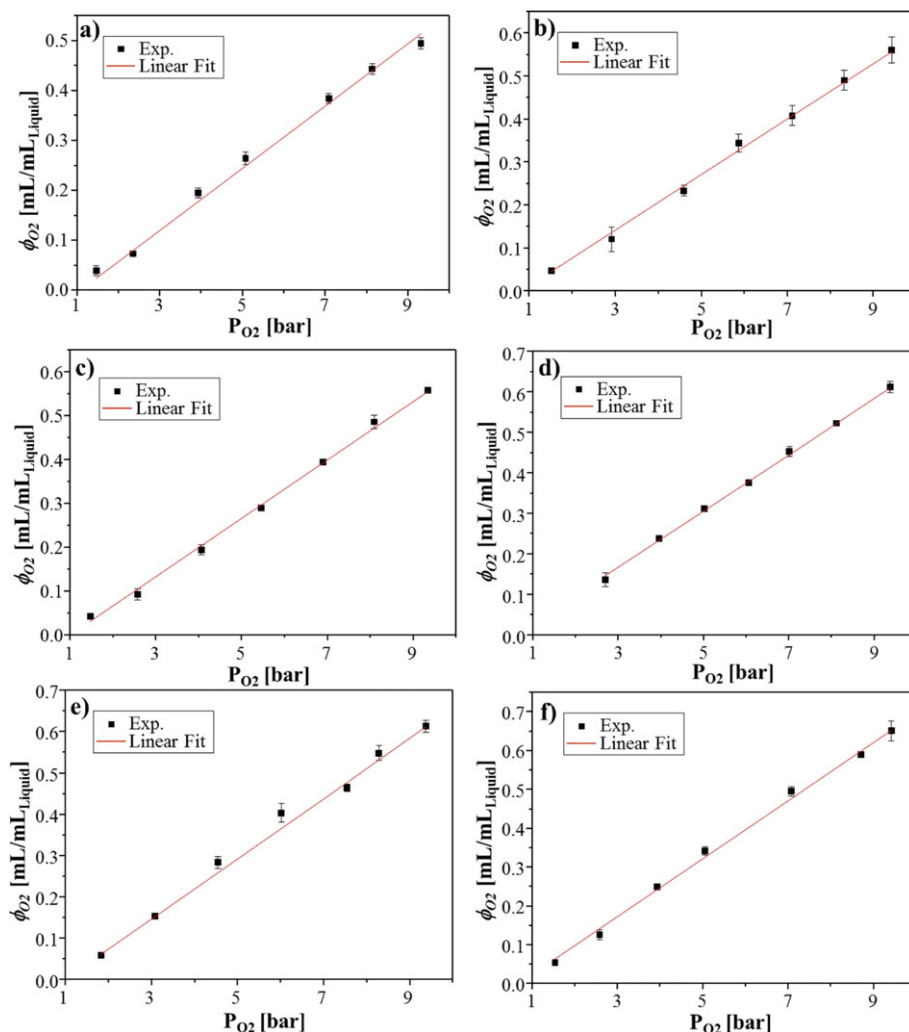

Figure 2. Amount of oxygen outgassed from liquid (ϕ_{O2}) as a function of oxygen pressure (P_{O2}) for oxygen-toluene at (a) 298 K and (b) 348 K.

$$\ln(H) = \frac{228}{T} + 7.39 \qquad (4)$$

4 Conclusions

A novel apparatus for the measurement of oxygen solubility in toluene and benzyl alcohol by a semipermeable Teflon AF-2400 tube-in-tube membrane contactor is introduced. The measured oxygen solubility in toluene is consistent with literature data, proving the reliability of this method. The oxygen solubilities in toluene and benzyl alcohol were both found to increase with temperature. However, the oxygen solubility in benzyl alcohol was much lower than that in toluene which has implications for accurate reactor design for aerobic oxidation of alcohols.

It is important to measure solubilities in the solvents/substrates employed in the actual reactions since using the solubilities of similar, but not identical, components can lead to errors in reactor design. As the Teflon AF-2400 membrane is highly permeable to other gases such as carbon monoxide and hydrogen, this method is not limited to oxygen and organic solvents but is generally applicable for measurement of other gas solubilities in a wide range of liquids.

Figure 4. Amount of oxygen outgassed from liquid (ϕ_{O2}) as a function of oxygen pressure (P_{O2}) for oxygen-benzyl alcohol at (a) 298 K, (b) 313 K, (c) 333 K, (d) 353 K, (e) 373 K, (f) 393 K.

obtained with correlation coefficient $R^2 = 0.987$. Thus, the correlation between Henry's law constant and temperature for the oxygen/benzyl alcohol system can be described by:
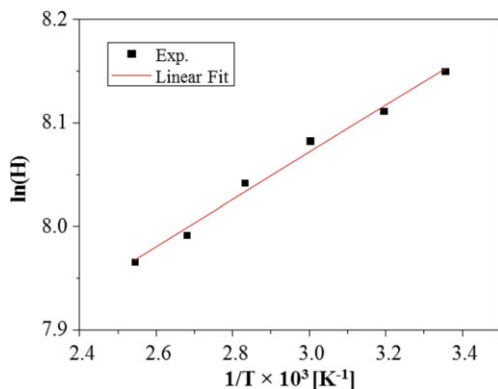
Figure 5. Henry's law constants (bar) for oxygen in benzyl alcohol as a function of temperature.

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