Measurement and prediction of oxygen solubility in post-combustion CO_2 capture solvents

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ABSTRACT

This work aims to understand oxygen solubility in pure and aqueous amine solvents for CO_2 capture. Commercially available dissolved oxygen sensors were studied to evaluate whether these can be used for measuring oxygen solubility in the carbon capture processes. It also aims to understand the possible discrepancies from realistic concentrations of oxygen when using a dissolved oxygen sensor. Two independent measurement principles were used for this purpose, both electrochemical and optical. Furthermore, a Winkler titration method was used to aid the validation of the sensors as well as understanding salting-out effects. A simple model for predicting oxygen solubility in CO_2-loaded ethanolamine solutions was made, which also has potential for predicting oxygen solubility in other loaded amine solutions.

The results of the study show that dissolved oxygen sensors may be applied for measurement of oxygen concentrations in amine solutions and that different amines and different concentrations in water only show small variations in oxygen solubility. The sensors may also be used in CO_2-loaded amine solutions, but here the increased conductivity of the solution may give a higher measured concentration of oxygen, than it is in reality. In ethanolamine, the consumption of oxygen is faster than the mass transfer of oxygen from gas to liquid phase, giving lower concentrations of oxygen than it should be in absence of a chemical reaction between oxygen and amine.

1. Introduction

The capture and storage of CO_2 from large emission sources (CCS) has to play a key role for reaching the target of not exceeding 1.5 °C increase of global average temperatures, concludes the Intergovernmental Panel on Climate Change (IPCC) in their report from 2018 (Rogelj et al., 2018). CCS allows for carbon (in form of CO_2), that would otherwise be released to the atmosphere and contribute to global warming, to be returned underground to safe and permanent storage. There are many studied technologies for CO_2 capture and of those, flue gas scrubbing with liquid amine solvents is one of the most mature technologies (Kohl and Nielsen, 1997; Leung et al., 2014; Rochelle, 2009). Liquids have inherent gas absorption properties and can physically absorb gases to some extent (Battino and Clever, 1966). Solvents with amine functions are, however, also chemically reacting with some gases, among these CO_2. The amines can more selectively, and in higher concentrations than physical gas absorption, bind the gas molecules. In this process, a solvent reversibly binds CO_2 at low temperatures in an absorber column and is released at high temperatures in a desorber column.

Because the reaction is reversible, the amine solution is circulated and reused continuously. The harsh operational conditions to which the solution is subjected; contact time with all flue gas components and construction material, as well as high temperatures in the desorber, can lead to amine degradation over time (Gouedard et al., 2012; Mazari et al., 2015; Meisen and Shuai, 1997; Reynolds et al., 2016). Oxidative degradation, the degradation that occurs in the presence of oxygen is a complex problem that can lead to corrosion, solvent and equipment replacement costs, and interruption of operation time (Dhingra et al., 2017; Goff and Rochelle, 2004; Rieder et al., 2017). For oxidative degradation reactions to take place they require presence of oxygen (O_2), and the main source for oxygen is the gas phase molecular oxygen

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present in the surrounding air or in the flue gas. It is commonly assumed that most of the oxidative degradation reactions take place in the absorber column where the oxygen concentration is the highest, because this is where the solvent is in contact with the flue gas and the temperature is the lowest in the process (da Silva et al., 2012).
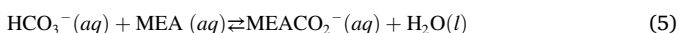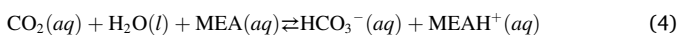
Laboratory experiments, where oxygen rich gas has been bubbled through aqueous amine solutions, have shown that there is a correlation between the amount of oxygen and the amount of oxidative degradation observed; increasing the oxygen pressure leads to increased rate of oxidative degradation (Supap et al., 2001; Vevelstad et al., 2016). Further, post combustion CO_2 capture pilot studies have shown that the loss of amine, caused by degradation into other compounds, increases linearly with the concentration of oxygen in the treated flue gas (Léonard et al., 2015). As a means of avoiding or limiting the extent of oxidative degradation, addition of oxygen scavenging compounds is a proven and commercially available method of reducing oxidative degradation in carbon capture plants (Fytianos et al., 2016; Léonard et al., 2014; Supap et al., 2011; Veldman and Trahan, 1997). These scavengers react stoichiometrically with dissolved oxygen and reduce the occurrence of oxidative degradation in the amine solution. However, another issue arises when the scavenger molecules are used up and removal of used-up scavenger, as well as addition of fresh scavenger has to be performed (Léonard et al., 2014). Together with this, undesired side effects such as foaming and cross-reactions with the solvent or other products can also occur with the direct contact of the solvent with the scavenger, as has been observed with corrosion inhibitors and other additives (Chen et al., 2011; Thitakamol and Veawab, 2008). To simplify operation of the carbon capture plant, a simpler way of eliminating molecular oxygen and thereby avoiding oxidative degradation would be preferred.

Because experimental observations show that oxygen pressure plays an important role in degradation, oxygen solubility is also a parameter in models attempting to predict oxidative solvent degradation (Pinto et al., 2014) under the assumption that its solubility in amines is similar to that of water.

The solubility of oxygen and other gases in non-reactive liquids is an inherent property and it depends on partial pressure of the gas and the temperature, as described by Henry's law given in Eq. 1

$$H^{cp} = \frac{C_l \cdot R \cdot T}{C_g} \qquad (1)$$

where Henry's law constant (H^{cp}) is correlated to the liquid-phase (C_l) and gas phase concentrations (C_g) of the gas component (in this case O_2), as well as the ideal gas constant (R) and temperature (T) (Henry, 1832).

$$O_2(g) \rightleftarrows O_2(aq) \qquad (2)$$

$$CO_2(g) \rightleftarrows CO_2(aq) \qquad (3)$$

$$CO_2(aq) + H_2O(l) + MEA(aq) \rightleftarrows HCO_3^-(aq) + MEAH^+(aq) \qquad (4)$$

$$HCO_3^-(aq) + MEA(aq) \rightleftarrows MEACO_2^-(aq) + H_2O(l) \qquad (5)$$

In addition to the physical solubility of gases (Eq. 2 and 3), CO_2 will chemically react with the amine in the solution. Depending on the type of amine, different reaction products are formed. For instance, a primary amine like ethanolamine (MEA) forms carbamate and protonated MEA ($MEACO_2^-$ and $MEAH^+$, Eq. 4 and 5) when reacting with CO_2, while tertiary amines form (bi)carbonate and protonated amine species (Danckwerts, 1979; Puxty and Maeder, 2016). Bicarbonate (HCO_3^-, Eq. 4) is also formed in reaction with water. Carbamates, as well as bicarbonate, are ionic species which will change the properties of the solution when formed from non-ionic compounds, a factor that influences oxygen solubility, known as a "salting in" or "salting out" effect (Schumpe et al., 1978).

The existing techniques for the quantification of dissolved oxygen include Winkler titration (Montgomery et al., 1964; Winkler, 1888), by means of gas chromatography in a molecular sieve column with thermal conductivity detection (GC-TCD) (Park and Catalfomo, 1964) and using electrochemical (polarographic) dissolved oxygen sensors. The titration method described by Winkler in 1888 is very accurate for aqueous samples with low or no alkalinity but is not directly applicable for the titration of amines. Quantification using an electrochemical sensor is a highly desirable method for industrial applications (Rooney and Daniels, 1998; Wang et al., 2013); it offers a fast, cheap and direct measurement that can easily be coupled online in the gas sweetening process. One of the challenges of the dissolved oxygen sensors is however the ionic strength of the solutions, which increases the conductivity and thereby enhances the electrochemical signal perceived by the sensor. The effect that the increased ionic strength has on the dissolved oxygen sensors is experimentally investigated in this work and compared to the predictions of the Schumpe model for gas solubility in aqueous electrolytes. Membrane transport of liquid or gas phase oxygen to the electrode of the sensor through the oxygen selective membrane of the electrochemical sensor is also studied in this work, to see if the presence of CO_2 impedes oxygen transport to the electrodes, as this type of membrane also is permeable to other small gas molecules (Bhattacharya and Hwang, 1997).

There are three main types of dissolved oxygen sensors, all designed for quantification of dissolved oxygen in water; polarographic, galvanic and optical. Polarographic, or "Clark" sensors (Clark, 1959), based on the same working principle as galvanic dissolved oxygen sensors, being selective reduction of O_2, but the galvanic type has a faster response time. The third type of dissolved oxygen sensor is optical, which relies on an oxygen-sensitive fluorescent dye, a light emitting diode and a photodetector to measure oxygen concentration in the solution. In this study sensors of both the galvanic, electrochemical and optical type have been used and compared.

The need for quantifying dissolved oxygen is not solely interesting for degradation modelling purposes mentioned above, but also for the development of oxygen removal technologies (Monteiro et al., 2018), where oxygen concentration needs to be quantified both before and after removal. The ideal analysis method should be direct (no sample processing), both decreasing the amount of work and sources of error. As already described, the solubility of oxygen is dependent on partial pressure and temperature, so that even small changes in either of these parameters, which is likely to happen during sample processing, could influence the measurement greatly. A further challenge for the measurements is the very low concentration range in which oxygen can be present. Any measurement method for dissolved oxygen needs to be sensitive enough to detect and quantify concentrations of oxygen in the low ppm-range (< 8 ppm).

This work has studied if different parameters, such as amine structure and concentration, as well as CO_2 loading, influence oxygen solubility. The methodological emphasis in this work was on electrochemical and optical dissolved oxygen sensors, because of their simple operation and potential for online measurements. Additionally, a promising modelling approach was used to predict oxygen solubility in CO_2 loaded amine solutions. The results of this study deepen the understanding of the extend of oxygen solubility in CO_2 loaded and unloaded amine solutions and how oxygen concentrations can be measured. The results also indicate that oxygen mass transfer is a limiting factor in the oxidative degradation of amines. The results of the study are an addition to the current understanding of oxidative degradation in amine-based CO_2-removal, as well as giving valuable information to those wanting to measure and understand oxygen solubility in the CO_2 capture process.

2. Materials and methods

2.1. Chemicals

Pure oxygen (O_2, N5.0) and carbon dioxide (CO_2, N5.0) gas were obtained from AGA and Linde Gas. and compressed air from in-house air compression systems at NTNU and TNO. Deionized water was obtained from local water deionization systems at NTNU and TNO. A further overview of chemicals used can be found in Table 1. All solutions were prepared gravimetrically.

2.2. Dissolved oxygen (DO) sensors

The solubility of oxygen was measured using two different electro-chemical dissolved oxygen sensors and one optical oxygen sensor, all designed for measurement of oxygen concentrations in water. The electrochemical dissolved oxygen sensors used are based on galvanic probes that give a measurable current proportional to the chemical reduction of O_2 on a cathode. The two different electrochemical sensors were used in this work were a HI-5421 Dissolved Oxygen and BOD Meter from Hanna Instruments, with a HI76483 Clark-Type polarographic probe and a handheld pHenomenal® OX 4100 H dissolved oxygen meter with a pHenomenal® OXY-11 polarographic probe, from VWR. A redox reaction gives a measurable current which directly correlates to the oxygen concentration in the solution. Effectively, the dissolved oxygen sensors measure the activity of O_2 in the solution which under ion-free conditions equals the concentration of O_2. Since salinity influences the activity coefficient of O_2, the sensors are provided with a correction for sodium chloride (NaCl) salinity. This correction factor is not applicable for other salts, as all ions have different salting-in or -out effects (Schumpe et al., 1978).

The optical dissolved oxygen sensor was a Memosens COS81D from Endress+Hauser. This was mainly used to validate the galvanic sensor working principle (electrochemical), to prove that a different principle (fluorescence quenching) also measures the same concentrations of oxygen. Each experimental section specifies which sensors have been used for the measurement and further details on their working principles are given in Appendix A.

2.3. Methods

Schematics of the experimental setups used in the various experiments are depicted in Fig. 1.

2.3.1. Experimental setup A: Oxygen solubility at ambient O_2 partial pressure

A 300 mL double-jacketed glass reactor (Fig. 1A), which was connected to a circulating combined heating and cooling bath, was filled with approximately 200 mL of the solution, which was cooled or heated to the experiments' starting temperature. When the desired temperature was achieved, compressed air was bubbled through the solution through a sintered gas dispersion tube, under magnetic stirring for at least 10 min. The gas dispersion tube was thereafter removed, for gas bubbles not to disturb the measurement. The magnetic stirring was maintained throughout the experiment, to ensure circulation of the liquid, maintaining the measured concentration around the probe head constant. The concentration of dissolved oxygen was recorded after the temperature stabilisation for each measurement point. Further measurements of dissolved oxygen were made at stable temperatures up to the upper operational temperature of the sensors.

2.3.2. Experimental setup B: Influence of CO_2 loading on oxygen solubility

A 300 mL double-jacketed glass reactor (Fig. 1B), connected to a circulating combined heating and cooling bath, was filled with approximately 200 mL of the solvent. A mixture of CO_2 and O_2, added through two mass flow controllers and subsequently mixed in a stainless steel tube, was suspended over the surface of the solution. A thermometer was inserted into the solution, the water bath adjusted to the desired temperature and temperature stability was awaited under a pure O_2 atmosphere, which was supplied through the tube suspended over the liquid surface. Once temperature stability in the liquid was reached, the dissolved oxygen sensor(s) was (were) inserted to the solution. A liquid sample for total inorganic carbon (TIC) analysis (section 2.6) was taken and simultaneously the first measurement of dissolved oxygen recorded. The gas flow from the tube above the liquid surface was adjusted to contain the desired ratios of CO_2 and O_2 and was kept constant throughout the whole experiment. A layer of parafilm was used to make a partial cover of the reactor, to assure that the gas phase over the liquid surface always contained the desired partial pressures of CO_2 and O_2.

Table 1

Short and trivial name, as well as structure, CAS number and key features of the chemicals used in the experiments.

| IUPAC name	Abbreviation	Chemical structure	CAS	Purity	Supplier	Features
phenylmethanamine	benzylamine		100−46-9	99 %	Aldrich	Primary aromatic amine
propane-1,2-diamine	1,2-DAP		78−90-0	99 %	Aldrich	Diamine
2-(2-aminoethoxy)ethanol	DGA		929−06-6	98 %	Acros Organics	Ether of a primary alkanolamine
2-(dimethylamino)ethanol	DMMEA		108−01-0	≥99.5 %	Aldrich	Tertiary alkanolamine
3-(methylamino)propane-1,2-diol	MAPD		40137−22-2	97%	Aldrich	Secondary alkane-diolamine
2,2'-(methylazanediyl)di(ethan-1-ol)	MDEA		105−59-9	≥99 %	Aldrich	Tertiary alkanolamine
2-aminoethan-1-ol	MEA		141−43-5	≥99.0 %	Sigma-Aldrich	Primary alkanolamine
ethane-1,2-diol	MEG		107−21-1	≥99.8 %	Sigma-Aldrich	Diol
2-(methyl)aminoethanol	MMEA		109−83-1	≥98 %	Aldrich	Secondary alkanolamine
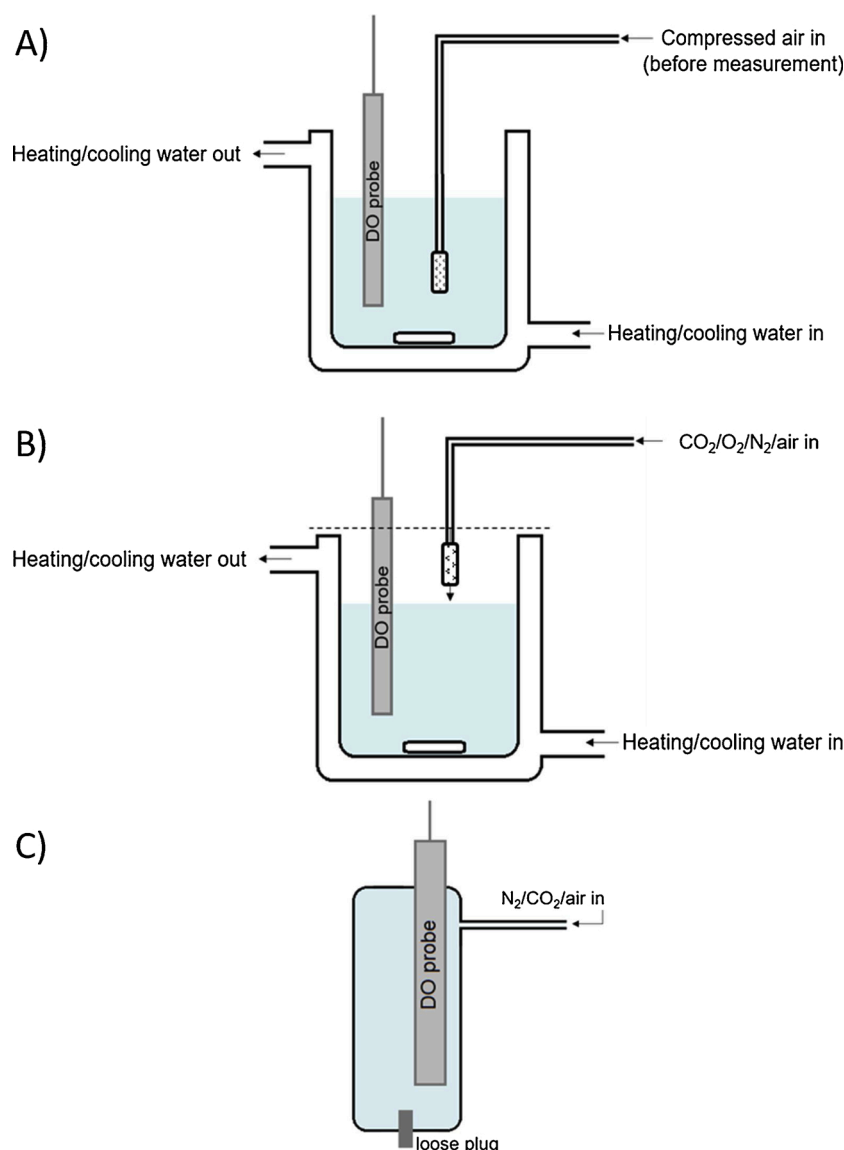
Fig. 1. Scheme for experimental setups A, B and C. Setup A and B are temperature controlled in a double-jecketed reactor, whereas C is only operated at room temperature. The gas distribution tube in setup B is moveable and maintained over the liquid surface during the measurment. Both setup A and B use magnetic stirring for mixing, whilst setup C relies on a constant flow of gas though the reactor, eliminating the need for futher agitation.

Liquid samples for TIC analysis were taken simultaneously as oxygen concentration recordings were made, approximately every 20 or 30 min.

2.4. Comparison of a galvanic and an optical dissolved oxygen sensor

Experimental setup A (Fig. 1A) was used for the following experiments with MEA, where oxygen solubility was measured with the galvanic VWR pHenomenal® and the optical Endress+Hauser COS81D dissolved oxygen sensors at room temperature with low loadings of 0.03 and 0.1 $mol_{CO2} \, mol_{MEA}^{-1}$. The solutions were sparged with compressed air before commencing the measurement of their oxygen concentrations, for reaching oxygen saturation at ambient pressure faster. Since MEA is commonly known as an unstable amine which degrades rapidly oxidatively, a very stable tertiary amine, MDEA, was also investigated. This was to see if a polarization of the oxygen selective membrane to inhibit oxygen permeation could occur with CO_2, which would be an operational problem with CO_2 present in the solutions. This experiment would also show if degradation rates can be assessed with the commercial sensors. A solution of 30 wt% MDEA (*aq.*) with a loading of 0.4 mol of CO_2 per mol MDEA was studied using experimental setup A (section

2.3.1). The solution was sparged with compressed air for 15 min after reaching temperature stability at 20 °C. Before measuring the oxygen concentration, the gas dispersion tube was removed, and the two sensors and a thermometer were inserted into the liquid. Temperature and oxygen concentration stability was awaited, before the first concentration and temperature point were noted. The liquid was slowly heated up and temperature and oxygen concentration measured by the two individual sensors were recorded regularly. Because of the high oxygen consumption rate, the same experiment could not be performed with MEA with CO_2 loading.

2.5. Study of possible CO_2 effects on dissolved oxygen sensors

2.5.1. Solubility of oxygen in water using three different gas phase compositions

Experimental setup B (Fig. 1B) was filled with deionized water and partly closed using parafilm. The water was then sparged with a specific gas composition, provided by two mass flow controllers, for 10−15 min at 20 °C, the temperature being kept constant at 20 °C using the combined heating and cooling bath. The gas distribution tube was then

placed above the liquid surface with gas still being distributed into the gas phase of the partly closed system and the Endress+Hauser COS81D dissolved oxygen sensor submerged in the liquid. Stability of the signal was awaited for 10−15 min and the temperature and concentration of oxygen measurement was noted. Three gas mixtures were studied using this setup; N_2 with air, CO_2 with air and pure air.
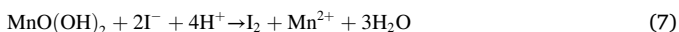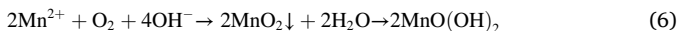
2.5.2. Gas phase oxygen measurement with the optical sensor

In experimental setup C (Fig. 1C), the 1.3 L glass reactor was added gas mixtures of different compositions, which were investigated using the Endress+Hauser COS81D dissolved oxygen sensor. Gas flows were controlled using two Bronkhorst® mass flow controllers, which supplied the gas at the top of the reactor and could escape through a small opening in the bottom of the reactor. The constant flow of the gas through the reactor ensured agitation around the sensor head, ensuring reliable oxygen solubility measurements. Stability of the signal was awaited for 10−15 min and the temperature and concentration of oxygen measurement was noted. Three compositions of air, CO_2 and N_2 were investigated, all at a room temperature of about 20 °C.

2.6. Analytical methods

A Shimadzu TOC-L_{CPH} in Total Inorganic Carbon (TIC) mode was used for the determination of the amount of CO_2 (as the only inorganic carbon species) in the solution. Amine titration with H_2SO_4 determined the exact amine concentration and from this, the exact CO_2 loading (α) of the solution was determined (Ma'mun et al., 2006). All samples were analysed twice, yielding a relative deviation of ≤2% for both methods, both comparing two parallel analyses and analysing standards of known concentrations.

Winkler titrations were performed using a HI-3810 Chemical test Dissolved Oxygen kit from Hanna Instruments. The quantification of dissolved oxygen relies on the reactions given in Eqs. 6–8.

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO_2\downarrow + 2H_2O \rightarrow 2MnO(OH)_2 \tag{6}$$

$$MnO(OH)_2 + 2I^- + 4H^+ \rightarrow I_2 + Mn^{2+} + 3H_2O \tag{7}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2S_4O_6^{2-} + 2I^- \tag{8}$$

An Agilent 7890A GC–MS was used in Electron Spray Impact ionization mode (ESI) with an *Equity™ – 1701 Fused silica capillary column* (30 m ×0.25 mm film thickness) and helium as the carrier gas. The quantification of dissolved oxygen was performed by a triple quadrupole mass spectrometer, by Single Ion Monitoring (SIM) of the fragment and molecular ions of oxygen, $m/z = 16$ and $m/z = 32$. These ions appear in the very start of the chromatogram, before any other compounds elute.

2.7. Modelling

The solubility of O_2 in CO_2-loaded and unloaded 30 wt% MEA solutions and concentrated NaCl solutions was estimated using the model of Weisenberger and Schumpe (1996). The model is suitable for predicting gas solubility into electrolyte solutions with concentrations up to 2−5 kmol m^{-3} and has been widely used in the literature. (Chatenet et al., 2000; Haug et al., 2017; Knuutila et al., 2010). The model expression is given in Eq. 9.

$$\log\left(\frac{C_{G,0}}{C_G}\right) = \Sigma(h_i + -h_G)c_i \tag{9}$$

In the equation $C_{G,0}$ and C_G are the gas solubility in water and in the electrolyte solution, respectively, h_i is the ion-specific parameter, h_G is the gas-specific parameter and c_i is the concentration the ion. The temperature dependence of the gas-specific parameter is given in Eq. 10.

$$h_G = h_{G,0} + h_T(T - 298.15 \text{ K}) \tag{10}$$

here $h_{G,0}$ is a gas-specific parameter, h_T is a gas-specific parameter for the temperature effect and T is temperature.

In this work, the solubility of O_2 in water, $C_{O_2,0}$ with unit mol dm^{-3}, was determined using the correlation given in Eq. 11 proposed by Xing et al. (2014). In the equation p_{O_2} is the partial pressure of O_2 above the solution,

$$C_{O_2,0} = \frac{55.56 p_{O_2}}{exp\left(3.71814 + \frac{5596.17}{T} - \frac{1049668}{T^2}\right) - p_{O_2}} \tag{11}$$

The ion concentrations in CO_2 loaded 30 wt% MEA (*aq.*) solutions were determined from NMR speciation data reported by Böttinger et al. (2008) and density data needed to convert mole fractions to molar concentrations were taken from Hartono et al. (2014).

The gas-specific parameter for oxygen in Eq. 9 are reported in literature. However, since the ion-specific parameters for protonated MEA (h_{MEAH^+}) and carbamate (h_{MEACOO^-}) were unknown, they were determined by fitting Eq. 9 to experimental nitrous oxide (N_2O) solubility data for CO_2 loaded 30 wt% MEA (*aq.*) solutions at 40 °C reported by Hartono et al. (2014). Since N_2O does not react chemically with the amine, it offers data for only the physical absorption in the liquid phase, which is then used to calculate the ion specific parameters. The Henry's law constant for N_2O in water ($H_{N_2O,W}$) was determined using the correlation given in Eq. 12, provided by Penttilä et al. (2011), and the partition coefficient expressed in Eq. 13 was calculated to be used as the $C_{G,0}$ value for N_2O at 40 °C.

$$H_{N_2O,W} = exp\left(158.245 - \frac{9048.596}{T} - 20.860 \ln T - 0.00252T\right) \tag{12}$$

$$m = \frac{RT}{H} \tag{13}$$

3. Results and discussion

3.1. Schumpe model and parameter fitting for estimation of oxygen solubility

The Schumpe model was used to represent the solubility of oxygen into water and salt solutions using parameters from literature. However, the model can also be used to predict oxygen solubility of aqueous amine solutions, using data for physical solubility of N_2O and speciation in CO_2 loaded solution. A theoretical prediction of oxygen solubility in loaded amine solutions, based on the effects of the ionic species in the solution has not yet been made for MEA. Using the literature and fitted ion specific constants given in Table 2, the predicted shown in Fig. 2 were calculated, proving that the model can accurately represent the N_2O solubility in loaded 30 wt% MEA. The constants needed for calculating the O_2 and N_2O solubility into CO_2 loaded 30 wt% MEA (*aq.*) solutions and in concentrated NaCl solutions are given in Fig. 2. The performance of the model to predict O_2-solubility using the fitted parameters will be

Table 2
Parameters for Eqs. 1 and 2. The $h_{T,i}$ value for O_2 is valid from 273 K to 353 K and that of N_2O is valid from 273 K to 313 K.

| Parameter	Unit	Value	Reference
h_{MEAH^+}	m^3 kmol^{-1}	0.0133	This work
h_{MEACOO^-}	m^3 kmol^{-1}	0.1284	This work
$h_{HCO_3^-}$	m^3 kmol^{-1}	0.0967	(Weisenberger and Schumpe, 1996)
h_{Na^+}	m^3 kmol^{-1}	0.1143	(Weisenberger and Schumpe, 1996)
h_{Cl^-}	m^3 kmol^{-1}	0.0318	(Weisenberger and Schumpe, 1996)
$h_{G,0,N_2O}$	m^3 kmol^{-1}	−0.0085	(Weisenberger and Schumpe, 1996)
$h_{G,0,O_2}$	m^3 kmol^{-1}	0	(Weisenberger and Schumpe, 1996)
h_{T,O_2}	m^3 kmol^{-1} K^{-1}	−0.000334	(Weisenberger and Schumpe, 1996)
h_{T,N_2O}	m^3 kmol^{-1} K^{-1}	−0.000479	(Weisenberger and Schumpe, 1996)
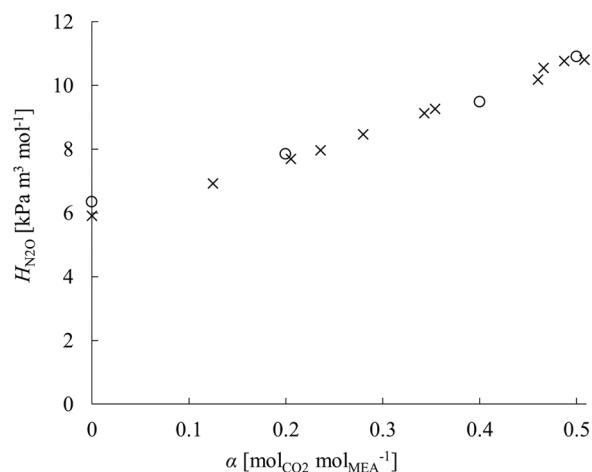
Fig. 2. The Henry's law constant for N_2O at 40 °C in MEA 30 wt% (*aq.*) solutions at different loadings. (○) Hartono et al. (2014) and (x) the model of Weisenberger and Schumpe (1996).

discussed in section 3.4.3 and Fig. 6.

3.2. Validation of the oxygen sensors with CO_2 unloaded solutions

Solubility of oxygen was measured in water (results in Appendix) and in 30 wt% (*aq.*) MEA by the three dissolved oxygen sensors was compared to available literature data. The results of this validation experiment can be found in Fig. 3. In MEA 30 wt% (*aq.*), the maximum absolute deviation between the dissolved oxygen sensors in this work was ± 0.6 mg L^{-1} (13 %, in the higher temperature range) and the maximum absolute deviation comparing the measured oxygen solubility to literature values from Wang et al. was 1.4 mg L^{-1} (13 %, in the higher temperature range). It should be noted that Rooney and Daniels (1998) and Wang et al. (2013) used polarographic dissolved oxygen probes for their dissolved oxygen measurements. Polarographic dissolved oxygen sensors use the same principle of detection as galvanic probes, therefore, the same oxygen selective cathode reactions apply.

All oxygen selective membranes are also selective towards CO_2, the effect of varying the gas phase composition between O_2, N_2 and CO_2 was studied in both water (described in section 2.5.1, results in Supplementary table 4) and gas phase (described in section 2.5.2, results in Supplementary table 5). No significant difference could be observed between measurements in mixtures of air and N_2, and air and CO_2. Replacing half the air with either of the two other gases, gave half the
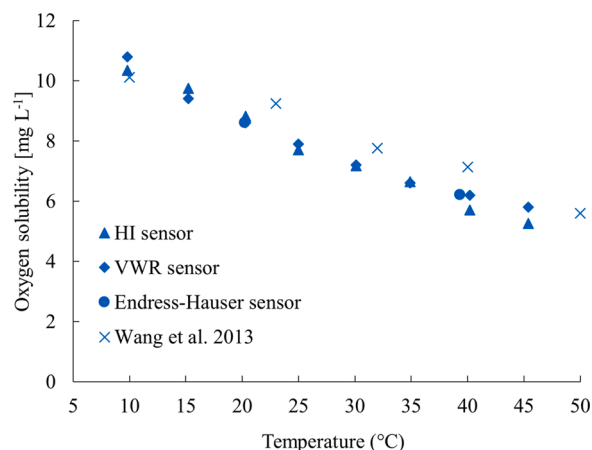

Fig. 3. Oxygen solubility of 30 wt% (*aq.*) MEA measured with three different dissolved oxygen sensors and compared to data from Wang et al. (2013). Solubility measured at $p_{O2} = 0.21$ atm.

concentration of oxygen measured with only air, although a small difference can be seen in the gas phase experiment, which can potentially be explained either by the sensor being slightly less accurate in air, or the experimental setup not being ideal for this type of experiment. Either way, dissolved or chemically bound CO_2 does not appear to influence the dissolved oxygen sensor.

Overall, the validation experiments and comparison with literature data for oxygen solubility in amine solutions and water, measured with comparable sensors, show a good agreement. This means that the sensors can be assumed to work in the same manner as other sensors from other brands and with slightly different working principles.

3.3. Winkler titration and GC–MS analyses

Oxygen solubility in selected solutions was also measured using Winkler titration. The quantification principles of dissolved oxygen using an electrochemical sensor and by performing a Winkler titration are different, but both are species-specific, measuring only dissolved oxygen. The electrochemical sensor gives a signal based on the current created from the cathodic reduction of O_2 to H_2O., while the titration relies on reduction of O_2 to form a MnO_2 salt. These independent methods show the same concentration of oxygen in pure water, but upon addition of salt, they deviate from one another. As Winkler titration method is not suitable for measuring the concentration of oxygen in amine solutions with a high pH, only aqueous solutions with NaCl or MEG because of their neutral pH, were analysed. Other disadvantages of a titration method in this case are the challenges related to sampling. Sampling will involve change of temperature and oxygen pressure, which in turn influences the oxygen solubility of the sample, additionally the amine solutions used for CO_2 capture are alkaline, a trait that is not compatible with the necessary acidification of the sample. All in all, these disadvantages make Winkler titration a bad alternative in industrial applications.

Further, as an attempt to find an additional independent validation method, a GC-MS study was performed for pure amine solutions, saturated with oxygen at normal atmospheric oxygen pressure ($p_{O2} \approx 0.21$ atm) by sparging with air. The possibility of using a GC-MS quantifying the molecule ions with m/z 16 and 32 in the pre-elution peak of a fused silica capillary column, was also tested in this work. Since the dissolved gas molecules are not retained in the column, the assumption that all the gas would elute before the rest of the sample was made, and indeed a pre-chromatogram peak containing only the m/z 14 and 28 (N^+ and N_2^+) in addition to 16 and 32 (O^+ and O_2^+) was seen. In different solvents, this peak's size varied, sometimes in orders of magnitude, in different amines and solvents and the reproducibility was poor (repeated analyses gave standard deviations >30 %). This validation attempt was therefore abandoned. A MS method for oxygen quantification could possibly become useful if it would be possible to retain the analytes in the chromatographic column in the future. If a GC method should be used, the results suggest that a molecular sieve (for gas separation) with a pre-column (for removal of solvent/liquid) GC-TCD method (Park and Catalfomo, 1964) would be recommended, although this equipment is not very common. Because of this, we were not able to access an instrument for testing the GC-TCD method in this work. It is also unsure whether this detection method would be able to quantify such low concentrations of oxygen.

3.4. Oxygen solubility in amine solutions

3.4.1. Oxygen solubility in different concentration of MEA (aq.)

The concentration of amine in water changes the physical properties of the liquid, such as viscosity and density. To study whether varying the concentration of amine also influences the oxygen solubility of the solvent, aqueous solutions of ethanolamine (MEA) were prepared and their oxygen solubility measured at different temperatures and compared to pure MEA and water.

The experiments were performed using the two electrochemical dissolved oxygen sensors and experimental setup A (section 2.3.1). The results given in Fig. 4 show a small deviation (17 % deviation and ±1.6 mg L^{-1} in the lower temperature range, 11 % and 0.6 mg L^{-1} above 20 °C) from the oxygen solubility in water. These observations agree with those of Wang et al. (2013), who concluded that the presence of MEA in an aqueous solutions does not significantly influence the concentration of dissolved oxygen compared to pure water. For further comparison, Henry's law constant (H^{cp}) was calculated from the measured solubility and pressure and these results show no significant difference from the Henry's law constants of water reported in literature (Supplementary Fig. 6 and Supplementary table 6).

3.4.2. Oxygen solubility in pure amine solvents

The structural variations in different amines suggest that the oxygen solubility could vary, as other chemical and physical properties of the solvents do. For the purpose of investigating this, amines with a relatively wide array of structural variation were subjected to the same conditions.

Oxygen solubility was measured and compared in structurally different amines at varying temperatures, using experimental setup A (2.3.1) and both electrochemical dissolved oxygen sensors. A primary (MEA), a secondary (*2-methylaminoethanol*, MMEA) and a tertiary alkanolamine (*2-(dimethylamino) ethanol*, DMMEA), as well as an aromatic amine (benzylamine), a diamine (*1,2-diaminopropane*, 1,2-DAP) and an ether of a primary alkanolamine (*2-(2-aminoethoxy) ethanol*, DGA) were studied, and the measured oxygen solubility of the amines are shown in Fig. 5. Pure amine solutions also show a very similar oxygen solubility to water, with very little variation. A study of amine viscosity and density showed that for alkanolamines, the oxygen solubility seems to decrease with increasing viscosity and density, an effect that could be related to the strength of hydrogen bonding in the solution. Detailed information about this can been found in the Appendix.

3.4.3. Influence of CO₂ loading on oxygen solubility

An increase in ionic strength, such as achieved by loading an amine with CO_2, leads to decreasing oxygen solubility. This effect is described by the ability of the ionic species to influence the dissolved oxygen activity coefficient and is commonly known as the "salting out effect", vice versa, ions that decrease the dissolved gas' activity coefficient can cause a "salting in effect" (Battino and Clever, 1966).

When an amine is used for CO_2 capture, the solution always contains CO_2, even at "lean" loadings. Therefore, pre-loaded solutions of MEA were studied at different temperatures. Aqueous solutions of MEA were loaded with pure CO_2 to obtain loadings in the range of 0.07−0.4 mol
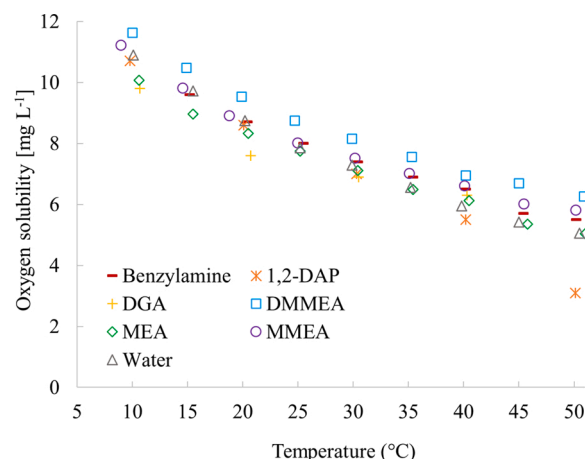
Fig. 5. Oxygen solubility of pure solvents as a function of temperature, all measured at p_{O2} = 0.21 atm.

CO_2 per mol amine. The amine and CO_2 concentrations were determined by amine titration and TIC analysis (section 2.6). The ability of the solutions to dissolve oxygen was investigated at different temperatures using experimental setup A (section 2.3.1) and both electrochemical dissolved oxygen sensors. The results given in Fig. 6 show decreasing oxygen solubility with increasing concentration of CO_2 in the solution. Oxygen concentration was also measured at the temperatures 30, 35 and 45 °C and these follow the same trend. For illustrative purposes, only the data for the temperatures which have been modelled are depicted in Fig. 6, whereas the other datasets are given in Supplementary Fig. 5. The oxygen concentration reaches a similar sudden drop in the data series recorded at 35 and 45 °C. Whether a drop or a linear decay in oxygen concentration is taking place already at 30 °C is unclear. These findings do, however, indicate that at realistic process conditions, which are above 35 °C, the oxygen concentration is likely to be severely influenced by rapid oxidative degradation of MEA already at typical lean loadings. While the modelling approach predicts the oxygen solubility into CO_2-loaded MEA solutions, what is measured here, is not representative of the physical solubilty of the solvent because oxygen is chemically consumed through degradation reactions with loaded MEA. It can be assumed that oxidative degradation already takes place at lower loadings, but that it seems that the degradation reactions are slow enough for the measured dissolved O_2 and the model predictions to be close to each other.

After observing the drastic drops in oxygen concentration with increasing CO_2 loading, a series of experiments where oxygen partial pressure was varied were performed. MEA solutions of 30 wt% (*aq.*)
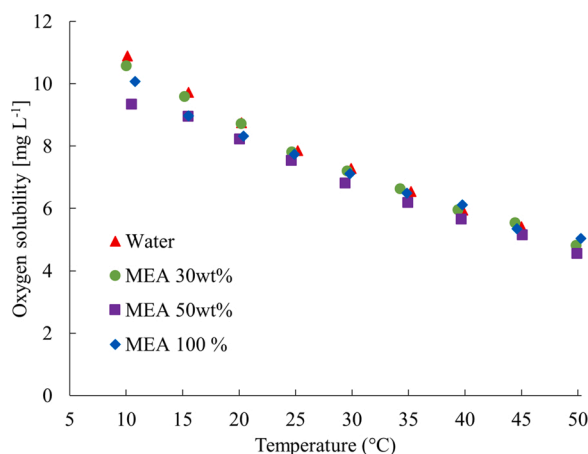

Fig. 4. Oxygen solubility in various concentrations of MEA at varying temperatures at p_{O2} = 0.21 atm. The shown oxygen solubility is the average of the measured solubility from the two different probes.
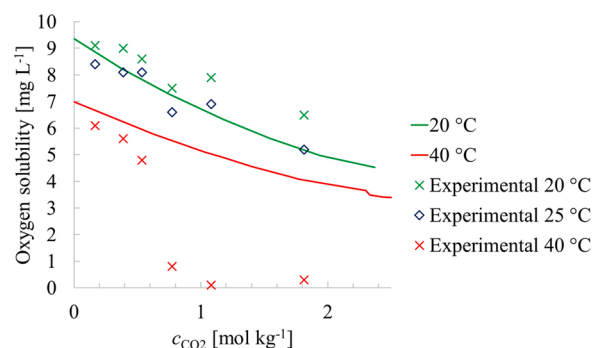

Fig. 6. With the adjusted ion parameters for MEAH$^+$ and MEACOO$^-$, as well as known values from Weisenberger and Schumpe (1996), the solubility oxygen in loaded MEA-solutions were predicted. The predicted solubilities are here compared to the measured solubilities at different temperatures, using the VWR pHenomenal® dissolved oxygen sensor.

were subjected to an O_2/CO_2 atmosphere of different, but in each experiment constant, ratios of the two gases, using experimental setup B (Fig. 1B and section 2.3.2) and the VWR pHenomenal® sensor. This led to the CO_2-loading increasing over time. All mixing ratios of O_2 and CO_2 gave a decreasing measured oxygen solubility in the amine solution with increasing loading (and time). Fig. 7 shows how the amount of oxygen in the surrounding atmosphere directly influences the solubility of oxygen in the solutions, but with increasing CO_2 loading the oxygen concentration in all cases suddenly drops. This drop indicates the point at which chemical reaction between amine and oxygen takes place faster than oxygen is transferred from the gas to the liquid phase.

Finally, to better understand the results, the concentrations of dissolved oxygen were measured in unloaded and loaded MDEA. The results are presented in Fig. 8. When compared to data presented in Figs. 6 and 7 for MEA loaded with CO_2, the same unexpected drop at higher loading was not seen in MDEA. Instead the apparent oxygen solubility increases from 7.6 mg L^{-1} in CO_2 free MDEA to 8.0 mg L^{-1} when the solution was loaded to 0.4 mol CO_2 per mol MDEA at 20 °C. The same behaviour was seen with both the optical and a galvanic sensor.

The fact that CO_2 loaded MDEA shows a measurable concentration of oxygen and loaded MEA not, supports the explanation of rapid consumption of dissolved oxygen in rapidly degrading amine solutions such as MEA. It can be assumed that dissolved oxygen sensors are able to give information about oxygen consumption rates, which again could give indications about the amines' oxidative degradation rates. For this to be fully understood, mass transfer rates of oxygen from gas to liquid phase must be known.

Furthermore, the solubility of oxygen in loaded MDEA is comparable to that of water or unloaded MEA. Since the dissolved oxygen sensor also measures the same concentration of oxygen regardless of N_2 or CO_2 being present in the gas phase in addition to O_2, it can be clear that CO_2 does not influence the measurement or causes membrane concentration polarization. As both the electrochemical and optical sensor measure the same oxygen concentrations in loaded solutions, we regard that both sensors are free from influence of other gases.

Finally, Fig. 6 also shows the modelling results based on the measured physical solubility of inert N_2O in loaded solutions of MEA by Hartono et al. (2014) and NMR speciation data of loaded MEA solutions (Böttinger et al., 2008). The oxygen solubility of solutions of MEA with CO_2 loading could be predicted using the model parameters given in Table 2 and Eqs. 9–11. As it can be seen in Fig. 6, where oxygen concentrations at different temperatures and CO_2 concentrations are compared to the concentrations predicted by the model, a slight deviation is observed for temperatures at 20 °C, where the measured concentration of oxygen is slightly higher than predicted. This effect can be explained by the increased conductivity and therefore amplification of
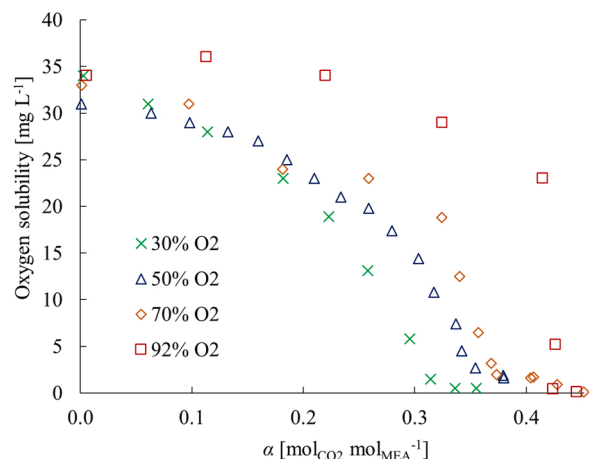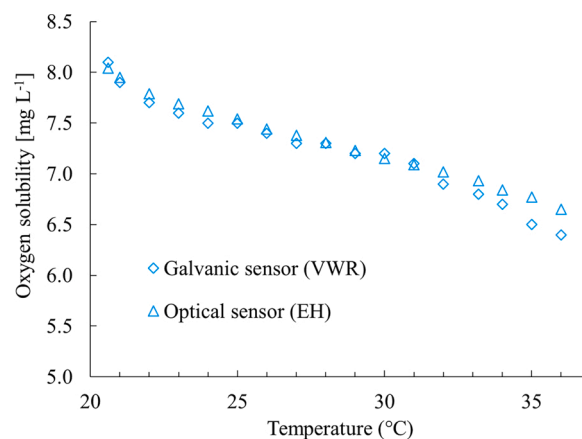

Fig. 8. The oxygen solubility of a solution of aqueous 30 wt% MDEA (*aq.*) with 0.4 mol of CO_2 per mol MDEA, measured with VWR pHenomenal® galvanic and the Endress+Hauser optical dissolved oxygen sensor at different temperatures.

the probe signal. At 40 °C, the deviation is however high, due to rapid oxygen consumption at this temperature.

Despite the signal being influenced by the ionic strength of the solution, the dissolved oxygen sensor method for determining oxygen concentrations of the amine solutions is the simplest, and only direct, of the tested methods. Of the few other existing options, the Winkler titration method is not suitable for use in alkaline solutions in addition to being indirect and involving sampling. Equilibrium cell experiments for measurement of dissolved oxygen requires high pressure, due to the low solubility of O_2. If the amines degrade rapidly in the presence of oxygen, the dissolved oxygen sensors do not actually measure the solubility of oxygen in the solution, as it is limited by the mass transfer from gas to liquid phase and the degradation rate of the amine. This goes especially for CO_2-loaded solutions of degradable amines like MEA and puts a large limitation to the applicability of dissolved oxygen sensors for determining the presence of liquid phase oxygen. Considering the results of this study, MEA appears to consume oxygen faster than fresh oxygen dissolves from the gas to the liquid phase, although there is a theortical inherent physical oxygen solubility in the solution, this is not measurable. This is not due to the measurement principle, but rather MEA's fast degradation or reaction rate in the presence of oxygen.

3.4.4. O_2 solubility in a degraded amine solution

A degraded amine solution contains a mixture which can contain alkaline amine, acidic and alkaline degradation products, heat stable salts, carbamate, dissolved metals and other ionic components. To study the effect of degradation products on oxygen solubility in an amine solution, a highly degraded amine solution was studied in the same manner as lean and loaded amines were studied in experimental section 3.4.1 to 3.4.3, with varying temperature of the solution. The degraded solution which was studied had been submitted to a three-week campaign of laboratory scale oxidative degradation and contained less than 1% of the original alkalinity (amine concentration). The degraded solution contained a total anionic HSS concentration of 0.75 mol kg^{-1}.

The oxygen solubility in 30 wt% (*aq.*) MAPD (CO_2 free) was measured with the VWR pHenomenal® dissolved oxygen sensor in experimental setup A (2.3.1) before and after strong oxidative degradation (CO_2 concentration < 1 g/kg). A complete loss of amine was found in the degraded solution, meaning that the solution primarily consisted of water and degradation compounds. The measurement results in Table 3 oxygen solubility neither increases nor decreases significantly with amine loss and increased concentration of degradation products.

Since there is no significant difference in the concentration of an unloaded (CO_2-free) amine solution and a highly degraded solution (also

Fig. 7. The solubility of oxygen decreasing with increasing CO_2 loading, when left in a gas atmosphere containing solely O_2 and CO_2 vol%) at 30 °C and 1 atm.

Table 3

Oxygen solubility of 3-methylamino-1,2-propanediol (MAPD, $\alpha = 0$) before and after laboratory scale oxidative degradation over a three-week period. Oxygen solubility was measured at $pO_2 = 0.21$ atm.

MAPD 30 wt% (*aq.*) fresh		MAPD 30 wt% (*aq.*) degraded	
Amine conc. [mol kg^{-1}]	2.85	Amine conc. [mol kg^{-1}]	0.0161
T (°C)	c_{O2} [mg L^{-1}]	T (°C)	c_{O2} [mg L^{-1}]
11.0	10.3	10.4	10.3
20.4	7.8	20.5	8.2
30.3	6.7	30.3	6.8
39.8	5.7	39.8	5.7
49.2	4.5	49.8	4.8

as good as CO_2-free), it can be speculated that the presence of degradation compounds in the form of heat stable salts have much less influence on the oxygen solubility than carbamate and protonated amine formation.

3.5. Significance of the results for the capture process

In an absorber column where CO_2 is absorbed from a flue gas, the liquid temperatures typically vary from 40 to 80 °C and as the solvent absorbs CO_2, the ionic strength of the solution increases. Furthermore, typical flue gas contains generally between 5 and 14 mol% oxygen (Feron et al., 2014; Hjelmaas et al., 2017; Lombardo et al., 2014; Moser et al., 2011a, b; Rieder et al., 2017). These factors lead to lower oxygen concentrations compared to those seen in this study, making the quantification of dissolved oxygen challenging, both because of upper operating temperature limits of the sensors and their limits of detection and quantification. The use of commercially available dissolved oxygen sensors made for water testing purposes can, however, be considered in industrial applications in amine solutions, if it has a relatively low oxygen consumption rate and the measurement takes place below the upper operating temperature of the sensor. Of the tested sensors, the optical dissolved oxygen sensor seems more capable of withstanding the alkalinity of the amine solutions than the other two, not suffering from neither corrosion nor other damage in the process, and may therefore be more suitable for dissolved oxygen measurements in a carbon capture facility.

Technologies for oxygen removal and oxidation inhibition in the amine solvent are being developed, to reduce the problems and costs related to oxidative degradation in amine scrubbers. These techniques generally base on oxygen removal by addition of oxygen scavengers, either by direct addition to the amine solution or indirect contact through a membrane barrier (Monteiro et al., 2018; Supap et al., 2011; Veldman and Trahan, 1997). Additionally a "salting out" method could potentially be applied, where an intentional increase of ionic strength of a solution is performed by addition of salts to decrease the overall oxygen solubility (Léonard et al., 2014). This approach will need careful testing, as the increase of salinity also may influence other solvent properties, like corrosivity, viscosity, density, cyclic capacity and heat of absorption.

Regardless of which of these techniques are being investigated or applied in industry, there is a need for a reliable method for quantifying the amount of oxygen in the solution before and after the removal operation, to evaluate the efficiency of the technology and to detect operational problems in the removal process if they occur. Ideally, the means of measurement should be direct, and preferably also online, to avoid unnecessary amounts of work and errors during sampling, in addition to giving a possibility for automated analyses. A dissolved oxygen sensor would be an ideal solution for direct measurement, but it would require the amine solution of choice to not consume dissolved oxygen faster than it is being transferred from the gas to the liquid phase,

to make any sense to measure at all. It also requires a sufficiently low detection and quantification limit of the sensor. Oxygen concentrations expected to be found in an amine scrubbing facility, where the temperature generally is high and the pressure of flue gas oxygen is low, are in the lower ppm range (at least <6 ppm, probably lower) and if the solvent is readily degradable, maybe even in the ppb-range. Since the apparent solubility given by the dissolved oxygen sensors are higher than reality, given the increased conductivity of the solution, it is possible that the sensor's sensitivity is increased and may be used in lower concentration ranges than expected. This effect will, however, need to be further studied and understood.

4. Conclusions

The results of the study show that commercially available dissolved oxygen sensors may be used to measure oxygen concentrations in amine solutions both in the presence and absence of CO_2. The increased conductivity of the solution when the amine has chemically bound CO_2 gives a slight amplification of the signal, which means that the actual concentration of oxygen is lower than measured. Oxygen solubility does not vary much in different solutions with and without amines. The factors influencing oxygen solubility the most are temperature, oxygen pressure and also the CO_2 loading. Amines with rapid oxidative degradation rates, such as ethanolamine, will consume oxygen from the solution faster than the oxygen transfer rate from gas to liquid phase. Measurement of oxygen concentrations in rapidly degrading amine solutions is therefore not useful. The actual oxygen concentration in these solvents will be very low, likely below the detection limit of any commercially available dissolved oxygen sensors (<<1 ppm). For amines which are stable under oxidative conditions, the sensors are fit for the purpose of measuring their oxygen concentrations.

The tested modelling approach seems both promising and realistic. However, for adjusting the Schumpe model, data on physical solubility of an inert gas in loaded solutions as well as ionic speciation are needed. Comparing model predictions to measured oxygen concentrations in solutions give indications of the solvent's degradation rate. The modelling approach can be a helpful tool when using oxygen solubility as a parameter for degradation modelling or when experimental determination is not possible.

The commercially available dissolved oxygen sensors may find an application as a fast screening method for the evaluation of oxidative stability of novel solvents, in addition to measurement of dissolved oxygen concentrations in chemically stable solvents.

CRediT authorship contribution statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijggc.2020.103205.

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