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Oxygen Solubility in Aqueous Amine Solvents with Common Additives Used for CO_2 Chemical Absorption

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Abstract

Major sources of anthropogenic CO_2 are power generation and transportation industries where researcher continue to explore CO_2 emission mitigation strategies as applied to these CO_2 sources through carbon capture, utilization, and sequestration (CCUS). The most mature CO_2 capture technology is post-combustion carbon capture (PCCC) using aqueous amine solutions/solvents, however solvent degradation and regeneration costs are slowing the widespread adoption of PCCC. Solvent degradation of the aqueous amine solutions is mainly caused from the temperature gradient between the absorber and stripper columns and common flue gas components such as SOx, NOx, and oxygen (O_2). The two main classifications of solvent degradation are thermal degradation, occurring when the amine reacts with itself at elevated temperatures and anaerobic conditions and oxidative degradation. Oxidative degradation reactions can occur from oxygen mass transfer and free radical oxidation. Metals, such as iron from the corrosion of steel structures used in industrial applications such as PCCC, can help to catalyze these reactions. Various oxidative degradation studies have shown how O_2 concentrations in flue gas and, to a lesser extent, temperature influence the extent of oxidative degradation.

Accurately measuring the O_2 solubility, commonly referred to as dissolved oxygen (DO), in a quick, continuous, and efficient manner in aqueous amine solvents should contribute to determine the effectiveness of mitigation strategies for oxidative degradation. Knowing that commercial PCCC amine solvents contain components beyond water, amine, carbonate species and CO_2, this investigation was conducted to determine the oxygen solubility changes of common aqueous amines solutions with commonly used and published solvent additives. The impact of carbon loadings with and without the additives was also examined. A commercial dissolved oxygen probe was used to measure the DO concentrations and compared them against standard Winkler Method titration values. The results show that antifoam shows minimal change in [DO]. MBT yielded lower DO values, and $NaVO_3$ showed a higher DO concentration due to interferences. These results indicate that most common amine solvent additives should be expected to minimally impact oxygen solubility and amine oxidative degradation.

Keywords: CO_2 capture; Dissolved oxygen; Oxidative degradation; Winkler Method

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1. Introduction

The increase in atmospheric CO_2 from anthropogenic sources in the past few decades raises global concerns about effects of climate change. [1] One research field, carbon capture, utilization, and sequestration (CCUS), attempts to discover a cost-effective and viable option for combating global climate change by removing atmospheric CO_2 and then sequestering or utilizing it. [2] The most researched CCUS technique, amine scrubbing post-combustion decarbonization, separates and captures CO_2 from a combustion process's flue gas producing a pure CO_2 stream. While the amine scrubbing process is well known, understanding the amine's solvent degradation and regeneration energy still challenges researchers.

Aqueous amine solvents can be a significant portion of the operating cost of CO_2 capture systems, with some costing over $40 per kg. If you consider a $40 per kg amine solvent that degrades at 0.5 kg per CO_2 ton captured, [3] this solvent will cost $20 per ton of CO_2 captured in terms of solvent replacement from degradation. If this solvent is used at a plant that captures 1 million CO_2 tons per year, then the solvent replacement will cost $20 million per year. This significant operating cost makes understanding and mitigating solvent degradation a key priority.

Typically, two mechanisms are used to describe degradation including from flue gas contaminants such as O_2 or SO_x and NO_x, and the variable heat gradients in the process. [4] In thermal degradation, a carbamate utilizes the stripper's high temperature and pressure atmosphere to react with itself forming product favored compounds. The other mechanism, known as oxidative degradation, involves O_2 or trace NO_x and SO_x gases becoming radicals through dissolved metal catalysis.

Previously studied mitigation methods for solvent degradation include thermal reclaiming, electrolysis, and ion exchange resins which help maximize the solvent's lifetime. [5] Some recently developed strategies such as N_2 purging [6] or with additive usage [7] show promise but are unproven for long-term treatment. Researchers seem preferential to these proactive strategies because they can stop degradation from occurring. Before deciding if the proactive strategies are effective and viable options, a reliable quantification method is needed. Since oxidative degradation starts with oxygen dissolving into the amine solvent and causing oxidation, accurately measuring dissolved oxygen (DO) can help to quantify the potential for oxidation within the solvent system.

According to ASTM D888[8], three standard analytical methods measure DO in water: a colorimetric titration known as the Winkler method, a polarographic DO electrochemical probe, and luminescence probe. The Winkler method determines O_2 solubility by using redox and acid-base reactions [9] whereas the polarographic probe determines DO by contact with an electrode through an oxygen permeable membrane. The luminescence probe uses dyes to determine DO and is sensitive to light [10] and was not used in this study. The Winkler method and the electrochemical probe are standardized for natural waters and therefore are unverified for aqueous amine solvents which have high pH (typically 10 to 12) depending on carbon loading and concentration.

With an understanding of the standard analytical methods for measuring DO, a commercially available DO electrochemical probe was validated with calculations determined from a modified Winkler method titration. The probe provided consistent and reliable results compared to the modified Winkler method indicating that this type of probe can be used to quantity oxidation in CCUS.

Nomenclature

DO	Dissolved Oxygen
CCUS	Carbon Capture, Utilization, and Sequestration
PCCC	Post Combustion Carbon Capture
HSS	Heat Stable Salts
EDA	1,2 -ethyldiamine

HDA	1,6 – hexadiamine
A2P	1-amino-2-propanol
2A1P	2-amino-1-propanol
DEA	diethanolamine
DMEA	dimethylethanolamine
MDEA	Methyldiethanolamine
NMEA	N-methyl-ethanolamine
2EAE	N-ethylamino-ethanol
MEA	ethanolamine
PZ	piperazine

2. Materials and Methods

2.1. Materials

Sigma Aldrich - 1,2-ethyldiamine (EDA), 2-amino-1-propanol (2A1P), Methyldiethanolamine (MDEA), N-methyl-ethanolamine (NMEA), N-(ethylamine)-ethanol (2EAE). TCI America - 1,6-hexadiamine (HDA), Acros Organics - 1-amino-2-propanol (A2P), Diethanolamine (DEA), Dimethylethanolamine (DMEA), Piperazine (PZ). Alfa Aesar - Monoethanolamine (MEA).

VWR - Manganese (II) sulfate ($MnSO_4$) ACS reagent (98%), Potassium iodide (KI) ACS reagent (99%), Sodium thiosulfate pentahydrate ($Na_2S_2O_3$•$5H_2O$) ACS reagent (99%). J.T. Baker's - Potassium iodate (KIO_3) ACS reagent (99.4% - 100.4%). Fisher Scientific - Potassium hydroxide (KOH) ACS reagent (88.5%), potato starch, and concentrated sulfuric acid (H_2SO_4), Acros Organics - sodium azide (NaN_3) (99%), Pharma-AAPER's - Chloroform (CCl_4). Pure CO_2 gas obtained from American Wielding and Gas.

2.2. Sample Preparation

The aqueous amines solvents, listed in **Fig. 1**, were prepared as described by Jorgensen *et al.* [11]

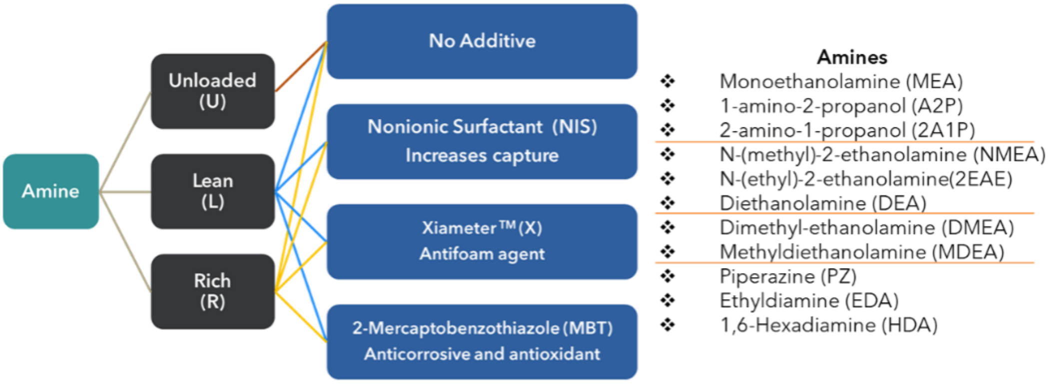


Fig. 1: Sample preparation flow chart and the amine solvents used for this work. The lines separate the amine list by structure. Primary, secondary, and tertiary amine solvents were prepared at 5M, diamines were prepared at 2.5M.

2.3. Electrochemical Dissolved Oxygen Probe

Electrochemical DO probes measure the signal produced by the oxygen reduction to hydroxide at a gold cathode separated from a solution by an oxygen permeable membrane. The current and O_2 partial pressure are proportional, and the converted current will readout a concentration. This study used a Thermo Scientific Orion Versa Star RDO/Dissolved Oxygen Temperature Module Dissolved Oxygen probe that is recommended for natural water ecosystems. A 10% random sampling of the DO probe's measurements in aqueous amine solvents were verified by triplicated Winkler method titrations. The DO probe calibration was conducted weekly by a two-point calibration using water saturated ambient air and zero oxygen standard (Ricca Chemical Co.) as recommended by the manufacturer. Deionized water and 5 wt.% sodium sulfite check standard solutions at 25°C and atmospheric conditions were used to verify calibration.

A water bath maintained at 25°C or 40°C target temperatures with a magnetic stir plate allowed the aqueous amine samples to continuously stir and remain open to ambient air. The measured DO concentration started with placing the DO probe into the aqueous amine samples. The probe equilibrated with the sample for, at minimum, five minutes ensuring the oxygen permeable membrane contacted the solution with no bubbles to provide stable readings.

2.4. Winkler Method

The redox reactions that comprise the traditional Winkler method (**Fig. 2**) start by manganese (II) hydroxide reacting with DO forming manganese (IV) oxide (equation 1). Next, add in potassium iodide under basic conditions which oxidizes iodide to iodine (equation 2). After, acidify the reaction and produce triiodide and a red-brown color (equation 3). A dark blue color appears with starch indicator and when titrated with thiosulfate reduces triiodide to iodide and a colorless solution (equation 4).

$$2Mn(OH)_{2(s)}+O_{2(aq)}\rightarrow 2MnO_{2(s)}+2H_2O_{(l)} \qquad (1)$$

$$MnO_{2\,(s)}+2I^-_{(aq)}+2H_2O_{(l)}\rightarrow 2Mn(OH)_{2\,(s)}+I_{2\,(l)}+2OH^-_{(aq)} \qquad (2)$$

$$I^-_{(aq)}+ I_{2\,(aq)} \rightarrow I^-_{3(aq)} \qquad (3)$$

$$I_{2(l)}+2S_2O_3^{2-}{}_{(aq)}\rightarrow S_4O_6^{2-}{}_{(aq)}+2I^-_{(aq)} \qquad (4)$$

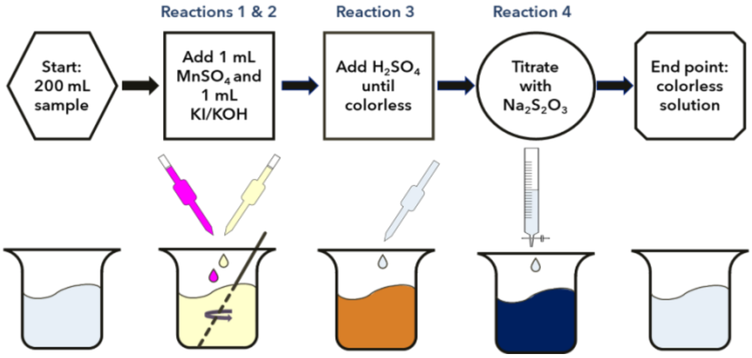


Fig 2. Diagram for the traditional Winkler method steps

Typically, an aqueous amine solvent's pH is between 9 and 11, and the exothermic reaction from adding acid to decrease the pH can increase the reaction temperature above iodine's boiling point and evaporating it. The decrease in iodine's concentration directly correlates to the calculated DO concentration. A backwards titration, proposed by

Wang *et al.* [12], allows iodine to stay in solution. The backwards titration adds in thiosulfate before the acid and where triiodide reduces to iodide a colorless solution with starch added in. When titrated with iodate, iodide oxides back to iodine (equation 5). Then using equation 6 DO mg L^{-1} can be calculated.

$$IO_{3\,(aq)}^{-}+5I_{(aq)}^{-}+6H_{(aq)}^{+}\rightarrow 3I_{2\,(l)}+3H_2O_{(l)} \qquad (5)$$

$$[O_2]=\frac{8000}{V_{Sam}}\left([Na_2S_2O_3]\times V_{Na_2S_2O_3}-6\times[KIO_3]\times V_{KIO_3}\right) \qquad (6)$$

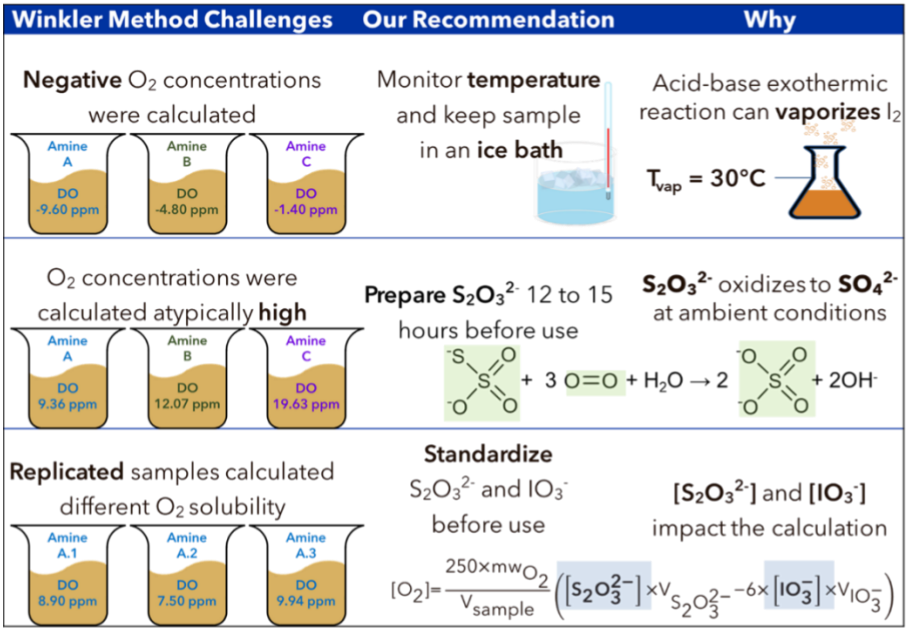
Following the method outlined in Jorgensen *et al.* [11] this study performed the traditional Winkler method for deionized water equilibrated with ambient air and the modified Winkler method for the aqueous amine solvents.

3. Results and Discussion

3.1. Challenges with the Winkler Method

Wang *et al.* [12] presented MEA's DO concentrations to model oxidative degradation. The one important aspect of this work related to O_2 solubility when adding sulfuric acid and its exothermic reaction causing iodine to evaporate (at ~30°C). [8] The authors explained that adding excess thiosulfate and performing a backwards titration using KIO_3 as the titrant will overcome iodine evaporation. To reproduce the backwards titration described by them, **Fig. 3** describes the challenges the modified Winkler method gave and our recommendations to use this method in amine solvents.

With an unloaded 5M amine solution, five replicated titrations using the modified Winkler method as Wang *et al.* [12] resulted in negative or low values that ranged between -9.60 mg L^{-1} and 3.20 mg L^{-1}. The negative calculated results indicated lower-than-expected iodate or iodine concentration due to temperature reaching above 40°C.



Winkler Method Challenges	Our Recommendation	Why
Negative O_2 concentrations were calculated Amine A DO -9.60 ppm Amine B DO -4.80 ppm Amine C DO -1.40 ppm	Monitor **temperature** and keep sample in an **ice bath**	Acid-base exothermic reaction can **vaporizes** I_2 T_{vap} = 30°C
O_2 concentrations were calculated atypically **high** Amine A DO 9.36 ppm Amine B DO 12.07 ppm Amine C DO 19.63 ppm	**Prepare $S_2O_3^{2-}$** 12 to 15 hours before use	**$S_2O_3^{2-}$** oxidizes to **SO_4^{2-}** at ambient conditions + 3 O=O + H_2O → 2 + $2OH^-$
Replicated samples calculated different O_2 solubility Amine A.1 DO 8.90 ppm Amine A.2 DO 7.50 ppm Amine A.3 DO 9.94 ppm	**Standardize** $S_2O_3^{2-}$ and IO_3^- before use	**[$S_2O_3^{2-}$]** and **[IO_3^-]** impact the calculation

$$[O_2]=\frac{250\times mw_{O_2}}{V_{sample}}\left(\left[S_2O_3^{2-}\right]\times V_{S_2O_3^{2-}}-6\times\left[IO_3^-\right]\times V_{IO_3^-}\right)$$

Fig 3: The challenges and recommendations when performing the modified Winkler Method.

Next, five titrations with unloaded 5M amine were performed with the reaction flask placed in an ice bath to manage the reaction temperature. These five samples resulted in high calculated O_2 solubility values that ranged between 9.36 mg L^{-1} and 19.63 mg L^{-1} with a 12.67± 4.10 mg L^{-1} average. The high calculated O_2 solubility indicated a higher-than-expected thiosulfate concentration. Upon further investigation, thiosulfate oxidizes in the presence of O_2 is producing SO_4^{2-} (equation 7). [8, 13] Therefore, to overcome thiosulfate oxidizing to sulfate, the thiosulfate solution was prepared 12 to 15 hours before use.

$$S_2O_3^{2-}{}_{(aq)}+2O_{2\ (aq)}+2OH^-_{(aq)}\rightarrow 2SO_4^{2-}+H_2O_{(l)}$$

Using both the ice bath and thiosulfate preparation modifications, an additional five titrations with unloaded 5M amine resulted in reasonable calculated O_2 solubility that ranged between 6.72 mg L^{-1} and 9.94 mg L^{-1} and an average of 8.32 ± 1.12 mg L^{-1}. The same five samples measured with the electrochemical DO probe resulted in a 6.93 ± 0.27 mg L^{-1} average. When comparing the two methods' O_2 solubility value, the Winkler method results in a higher O_2 solubility value and a high standard deviation. When looking closer into equation 6 slight deviations in the thiosulfate and iodate concentrations can cause significant change to the calculated O_2 solubility value. Therefore, accurate standardization of the thiosulfate and iodate concentrations can correct the Winkler method deviation and lead to more accurate O_2 solubility calculations.

Table 1: Modified Winkler method calculated DO values compared to electrochemical probe measurements after last modification

Sample	Winkler Method (*mg L^{-1}*)	Electrochemical Probe (*mg L^{-1}*)	Variance
1	6.06	6.63	
2	6.30	7.18	
3	5.54	7.20	
4	6.15	6.68	
5	6.75	6.96	
Average	6.16 ± 0.44	6.93 ± 0.27	-0.77

Finally, five unloaded amine samples were titrated with thiosulfate and iodate standardized from an adapted ASTM-1510 [14] producing a 6.16 ± 0.44 mg L^{-1} calculated O_2 solubility average with a range of 5.54 mg L^{-1} and 6.75 mg L^{-1}. Comparing the calculated modified Winkler method O_2 solubility with the measured electrochemical DO probe an observed difference of 0.77 mg L^{-1} as shown in **Table 1**.

3.2. Validation

With the modified Winkler method and the electrochemical DO probe giving comparable results for a single sample, the DO for a 5M monoethanolamine (MEA) solvent at unloaded (C/N = 0), lean loaded (C/N = 0.20), and rich loaded (C/N = 0.40) conditions were calculated using the modified Winkler method titration and measured with the electrochemical probe. The results, shown in **Fig. 4**, determine the titration calculated the O_2 solubility are in good agreement, with the probe showing only slightly higher values. One possible reason for this is the thiosulfate being added into the solution may have absorbed some O_2 from the air and resulting in a slightly higher calculated DO concentrations.

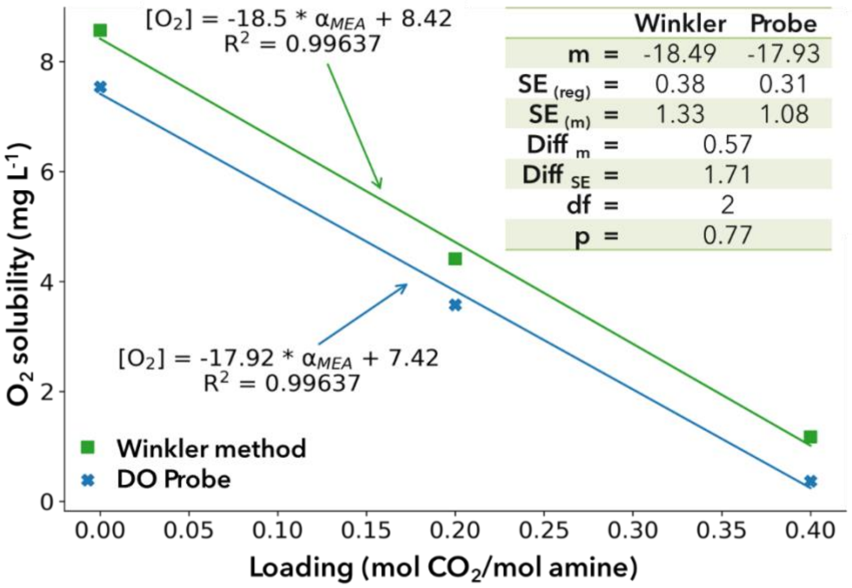


Fig 4: The O_2 solubility vs Loading for 5M MEA at unloaded, lean loaded, and rich loaded conditions

To further validate the electrochemical probe, eleven aqueous amine solvents at typical loadings found in carbon capture were prepared with and without four additives typically found in commercial application solvents. These amines were chosen based on structure (primary, secondary, tertiary, and diamines) and are solvents typically discussed in literature. Commercial amine solvents will contain additives to increase performance, or inhibit a technical challenge caused by the solvent or process. Common additives include a non-ionic surfactant (NIS), Xiameter ^{TM} (X) and 2-mercaptobenzothiazole (MBT). A 10% random sampling of the prepared solutions had the measured O_2 solubility by probe and compare to the calculated titration values.

The difference between the electrochemical DO probe and the modified Winkler method or variance for samples without additives, samples with NIS, Xiameter ^{TM}, and MBT are all within 1 ppm and presented in **Fig. 5**. All samples with Xiameter ^{TM} measured DO resulted in a higher deviation from the modified Winkler method than NIS and MBT samples, as the probe gave a lower result than the titration. The higher deviation from Xiameter ^{TM} could be due to the additive properties as it is an antifoam agent, it likely slowed down the decrease in pH during the titration and allowed the thiosulfate to capture more O_2 from the air. The further validation by the modified Winkler method to the electrochemical DO probe values shows confidence in the probe to produce accurate O_2 concentrations in the aqueous amine solvents with CO_2 and additives.

4. Conclusion

This study focused on the lessons learned during the Winkler method’s modification with aqueous amine solvent analysis and an electrochemical DO probe’s validation for amine scrubbing carbon capture purposes. The modified Winkler’s method lessons learned include iodine evaporating at 30°C, thiosulfate oxidizing when exposed to ambient atmosphere, and the importance of accurate thiosulfate and iodate reagent concentrations. In addition to the backwards titration, the temperature sensitivity was aided using an ice bath removing excess heat produced by the acid and base reaction allowing iodine to stay in solution. Thiosulfate oxidizing when exposed to ambient atmosphere was overcome by preparing fresh thiosulfate no more than 12 to 15 hours before each titration. The sensitivity of iodate and thiosulfate concentrations in the modified Winkler method’s calculation was solved by standardizing the solutions before use.

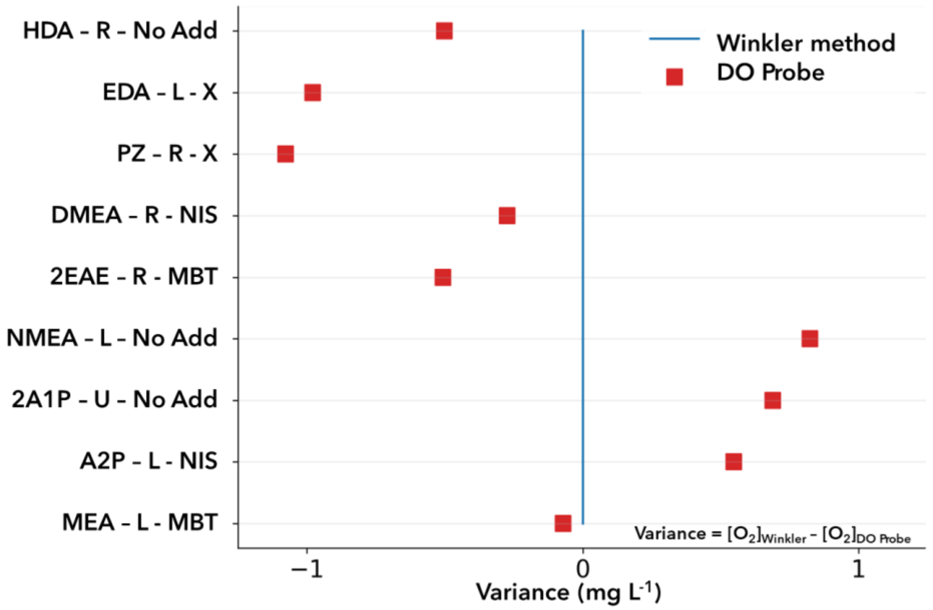


Fig 5: The variance between electrochemical DO probe and modified Winkler method for a random sampling of the samples discussed in Jorgensen *et al*. [11]

The electrochemical DO probe validation included a 5M MEA aqueous amine solvent at different loadings. The measured probe values were compared to the calculated titration values and resulted in similar values thus giving confidence in the probe's measurements. The probe was further tested with a random sample of different amines, at different loadings, with and without common additives used in amine scrubbing carbon capture. The difference between the two methods were within 1 ppm for the different amines, loadings, and additives indicating that the probe can confidently measure commercial amine solvent's oxygen solubility quickly and efficiently.

Acknowledgements

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