

SPRING 1998

# PETROLEUM TECHNOLOGY QUARTERLY

REFINING ★ GAS PROCESSING ★ PETROCHEMICALS

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**Peter C Rooney and Danny D Daniels**  
**GAS/SPEC Technology Group**

### INEOS LLC

As part of a Federal Trade Commission mandated remedy to the merger of The Dow Chemical Company and the Union Carbide Corporation, INEOS plc was able to purchase both Dow's Ethanolamines and GAS/SPEC MDEA-based specialty amine businesses. This purchase became effective on February 12, 2001.

INEOS LLC was set up as the newly acquired company, which includes the GAS/SPEC Technology Group. All the key Ethanolamines and GAS/SPEC personnel were retained by INEOS LLC. All GAS/SPEC products, technology and know-how became the exclusive property of INEOS on a global basis.

# Oxygen solubility in various alkanolamine/water mixtures

Oxygen is known to cause colour and degradation in alkanolamines used in gas treating, but so far no studies have been reported measuring oxygen solubility in these systems. This article examines the solubility in water and alkanolamine/water mixtures at temperatures between 60 and 180°F

Peter C Rooney and Danny D Daniels  
The Dow Chemical Company

The solubility of oxygen in a wide variety of substances is known. The most studied system is most likely dissolved oxygen in water at atmospheric pressure. Oxygen solubility has been performed by physical measurements using manometric or volumetric methods,<sup>1</sup> gas chromatography,<sup>1</sup> and mass spectrometry.<sup>1</sup> Electrochemical methods using some version of the Clark electrode or polarography have been reported.

Chemical methods such as the Winkler method (based on iodine liberation in the presence of divalent manganese followed by titration with thiosulphate), modifications of the Winkler method, and a colorimetric

method based on the oxidation of indigo-carmin have also been reported.

In this article, the solubility of oxygen in water and various alkanolamine/water mixtures at temperatures from 60–180°F is reported. The alkanolamine/water mixtures chosen in this study are the most common generic solvents used in the gas treating industry to remove acid gases (CO<sub>2</sub> and H<sub>2</sub>S) from natural gas and synthesis gas. They are: 50 wt% methyldiethanolamine (MDEA), 30 wt% MDEA, 30 wt% diethanolamine (DEA), 20 wt% monoethanolamine (MEA) and 50 wt% diglycolamine (DGA).

Although oxygen has long been known to cause colour and degradation in alkanolamines used in gas treating, to

date there have been no studies reported that measures oxygen solubility in these systems. This data will help quantitatively and predict the effect that oxygen has on the degradation of alkanolamines in customer gas plants.

## Experimental details

The alkanolamines (MEA, DEA, and MDEA) were produced by Dow and used without further purification. DGA (99+ per cent) was purchased by Aldrich. Distilled water was used as the water source for all experiments. Compressed air (21.3 per cent oxygen; ultra zero grade) was purchased from IWECO (Freeport, Texas). A certificate of analysis showed the air contained <1ppm CO, <1ppm CO<sub>2</sub>, <2ppm water, <0.1ppm hydrocarbons and <0.1ppm NO.

The dissolved oxygen probe used was a Mettler Toledo 120mm probe having a membrane with an exterior Teflon layer (Part No. 34 100 3045). Dissolved oxygen readings were made using a Mettler Toledo Model 4300 microprocessor-based oxygen transmitter.

Dissolved oxygen experiments were performed by sparging the compressed air through a Cole-Parmer 0–150sccm flow meter at a rate of 25sccm into 150mL of the solution to be studied, which was contained in a 250mL jacketed beaker. The solution was stirred with a magnetic stir bar while continually sparging with the compressed air. The temperature of the solution, adjusted using a GCA Precision R10 circulating bath, was monitored using a thermometer.

A polycarbonate cover with slits for the thermometer, air entrance and exit, and the dissolved oxygen probe was used on top of the beaker to prevent CO<sub>2</sub> in the atmosphere from entering the solution. Once the temperature was equilibrated, dissolved oxygen readings were monitored until they stabilised (usually about 10–15 minutes).

Dissolved oxygen measurements were corrected for the vapour pressure of water at each temperature (see under

## Comparison of dissolved oxygen against temperatures

Dissolved oxygen vs temperature at 101.325kPa and 20.95% oxygen using Equations 1 and 2 vs This Work

Temp °C	Temp °F	Dissolved oxygen (ppm) using Eq 1	Dissolved oxygen (ppm) using Eq 2	Dissolved oxygen (ppm) using This Work	% Error Eq 2 vs (this work)
0	32	14.74	14.78	–	–
5	41	12.92	12.94	–	–
10	50	11.46	11.48	–	–
15	59	10.29	10.31	–	–
15.5	60	10.18	10.19	9.98	2.06
20	68	9.34	9.36	9.23	1.39
25	77	8.56	8.59	8.37	2.56
30	86	7.92	7.96	7.65	3.89
35	95	7.40	7.43	7.24	2.56
40	104	6.97	7.00	6.68	4.57
45	113	6.62	6.63	6.20	6.48
50	122	6.34	6.34	5.86	7.57
55	131	6.10	6.09	5.65	7.22
60	140	5.92	5.88	5.47	6.97
65	149	5.78	5.71	5.34	6.48
70	158	5.68	5.57	5.14	7.72
75	167	5.61	5.46	5.16	5.49
80	176	–	5.38	5.08	5.58
82	180	–	5.36	5.01	6.53
85	185	–	5.31	–	–
90	194	–	5.27	–	–
95	203	–	5.24	–	–
100	212	–	5.26	–	–

Table 1

Results and Discussion heading below). No corrections were made for atmospheric pressure, which ranged from 14.60–14.73psia (755–762mm Hg).

**Results and discussion**

**Comparison of water solubility**

Battino (reference 1, pp1–6) compared over 40 papers with data on oxygen solubility in water. After comparing many data points, and rejecting data points that were beyond two standard deviations beyond the smoothed line, he came up with 149 points that had a fit of ±0.36 per cent at the middle of the temperature range from 273–348K.

The best fit for these 149 points gave:

$$\ln x_1 = -66.73538 + 87.47547 / (T/100K) + 24.45264 \ln (T/100K) \quad (1)$$

where  $x_1$  is the mole fraction solubility at 101.325kPa partial pressure of gas. Benson, Krause and Peterson (reference 1, p2) extended their work to cover the temperature range of 273–373K and obtained a standard deviation of ±0.017 per cent for their 37 data points at the midpoint of their smoothed line when the following best fit was used:

$$\ln k = 3.71814 + 5.59617 \times 10^3 / (T/K) - 1.049668 \times 10^6 / (T/K)^2 \quad (2)$$

where the fugacity  $f = kx_1$  and  $k$  is the Henry coefficient (at unit fugacity).

A comparison of dissolved oxygen using equation 1, equation 2 and the results of this work using the dissolved

Partial pressure water correction factors vs temperature, using Equation 5				
Temp °F	Temp °C	P (atm)	vol%	Correct'n factors*
32	0	0.006025	0.6025	1.006
41	5	0.008609	0.8609	1.009
50	10	0.012117	1.2117	1.012
59	15	0.016786	1.6786	1.017
60	15.5	0.017336	1.7336	1.018
68	20	0.023072	2.3072	1.024
77	25	0.031258	3.1258	1.032
86	30	0.041874	4.1874	1.044
95	35	0.055549	5.5549	1.059
104	40	0.07279	7.2879	1.079
113	45	0.094579	9.4579	1.105
122	50	0.121724	12.1724	1.139
131	55	0.155316	15.5316	1.184
140	60	0.196553	19.6553	1.245
149	65	0.246763	24.6763	1.328
158	70	0.307500	30.7500	1.444
167	75	0.380395	38.0395	1.614
176	80	0.467237	46.7237	1.877
180	82.2	0.510364	51.0364	2.042

\*Correction factor = 1/(1-P), where P is in atmospheres

Table 2

Comparisons							
Comparison of ppm dissolved oxygen at 101.325kPa and 20.95% oxygen for water vs various alkanolamine/water mixtures, using dissolved oxygen probe							
Temp °C	Temp °F	100% DI H <sub>2</sub> O*	50% MDEA	30% DEA	20% MEA	50% DGA	30% MDEA
15.5	60	9.98	10.61	9.76	10.29	9.86	10.43
20	68	9.23	9.83	8.90	9.48	8.96	9.57
25	77	8.37	8.90	8.31	8.61	8.08	8.79
30	86	7.65	8.04	7.59	7.85	7.56	8.04
35	95	7.24	7.34	7.14	7.22	6.94	7.43
40	104	6.68	7.04	6.65	6.65	6.55	6.94
45	113	6.20	6.51	6.22	6.21	6.16	6.54
50	122	5.86	6.08	5.87	5.98	5.77	6.13
55	131	5.65	5.80	5.42	5.78	5.66	5.85
60	140	5.47	5.58	4.86	.54	5.44	5.46
65	149	5.34	5.57	4.48	5.28	5.45	5.36
70	158	5.14	5.54	4.23	5.24	5.21	5.20
75	167	5.16	5.40	3.89	5.06	5.40	5.13
80	176	5.08	5.28	3.91	5.36	5.54	5.15
82	180	5.01	5.39	3.58	4.92	5.59	5.06

\*Measured with dissolved oxygen probe (this work).

Table 3

oxygen probe (mentioned earlier under Experimental details), after converting the mole fractions of dissolved oxygen to ppm dissolved oxygen using equation 3, is seen in Table 1. It is seen that the oxygen probe values obtained are between about 1.4–7.6 per cent lower than those obtained using equation 2.

$$\text{ppm dissolved oxygen} = \text{mole fraction} \times 32/18 \times 1000000 \text{ppm} \times 0.2095 \quad (3)$$

where 32/18 is the molecular weight of oxygen over water, and 0.2095 is for 20.95 per cent oxygen in air.

It is noted here that the ppm dissolved oxygen values obtained by the dissolved oxygen probe were corrected for the partial pressure of water and 20.95 per cent oxygen using equation 4.

$$\text{ppm dissolved O}_2 = \text{Probe ppm reading} \times \text{water correction factor} \times 20.95/21.3 \quad (4)$$

where the fraction 20.95/21.3 is the ratio of oxygen in air (20.95 per cent) compared to the per cent oxygen in the air cylinder used in these experiments (21.3 per cent). The partial pressure correction factor (Table 2) was obtained from the CRC Handbook of Chemistry and Physics (62nd edition, page D-168)

**Alkanolamine/water mixtures**

A comparison of the ppm dissolved oxygen measured using the dissolved oxygen probe in 50 per cent methyldiethanolamine (MDEA), 30 per cent diethanolamine (DEA), 20 per cent monoethanolamine (MEA), 50 per cent diglycolamine (DGA) and 30 per cent MDEA compared to DI water is shown in Table 3 and Figure 1.

In each case, corrections for water vapour pressure and the 21.3 per cent

oxygen used in these tests were performed.

Duplicate runs of the solubility of oxygen in 30 per cent DEA in water, compared to 100 per cent DI water, are shown in Table 4 and Figure 2. It is seen that the oxygen solubility in the 30 per cent DEA continues to drop much more dramatically from about 131°F up to 180°F compared to water and the other alkanolamines. There is good reproducibility between runs 1 and 2.

**Effect of pressure on oxygen solubility**  
Henry's law for dilute solutions states that under equilibrium conditions the fugacity (f) of a gas above a solution is proportional to the mole fraction of the gas in the liquid phase.<sup>1,2,3,4</sup>

Within the range of validity of the law, the Henry's constant,  $k$ , is independent of fugacity but varies only with temperature, and not with pressure. Benson et al<sup>5</sup> recommend that equations 5 and 6 be used to calculate the mole fraction oxygen solubility as a function of oxygen partial pressure at temperatures of 273–373K (32–212°F) and 373–563K (212–554°F), respectively.

In each case, the fugacity is assumed to be equal to 1,  $k$  is in atmospheres (atm) and temperature (T) is in Kelvin (K). These mole fractions of oxygen can then be converted to ppm dissolved oxygen using equation 7, where 32/18 is the molecular weight of oxygen over water, and the partial pressure of oxygen is in atmospheres.

$$\ln k = 3.71814 + 5.59617 \times 10^3 / T - 1.049668 \times 10^6 / T^2 \quad (5)$$

$$\ln k = -4.1741 + 1.3104 \times 10^4 / T - 3.4170 \times 10^6 / T^2 + 2.4749 \times 10^8 / T^3 \quad (6)$$

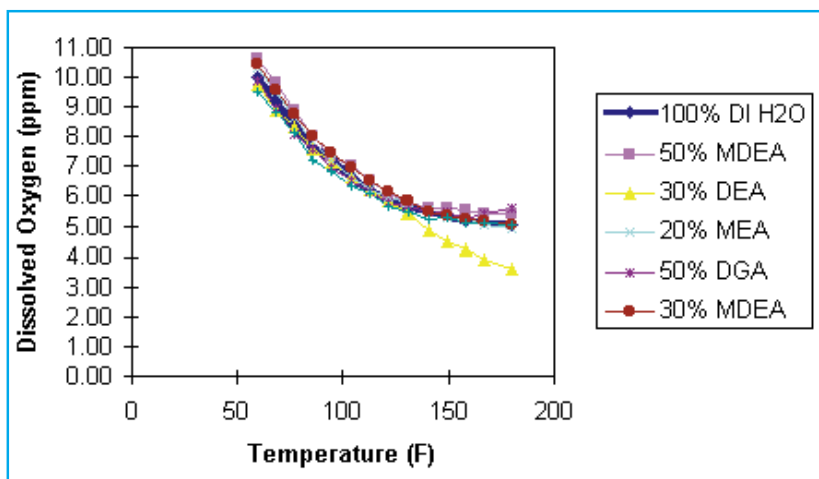


Figure 1 Comparison of ppm dissolved oxygen at 101.325kPa and 20.95% oxygen for water vs various alkanolamine/water mixtures, using dissolved oxygen probe

ppm dissolved oxygen = mole fraction  $\times$   $32/18 \times 1000000 \times$  oxygen partial pressure (7)

Figure 3 (using equations 5, 6 and 7) shows how oxygen solubility in water varies with oxygen partial pressure from 30–300°F. Note that in each case that oxygen solubility decreases with increasing temperature up to about 212°F, and then increases with increasing temperature.

Given how the oxygen solubility of the various alkanolamines was very similar to the solubility of oxygen in water at 1 atm, until additional experiments are performed to more accurately predict the solubility of oxygen in various alkanolamines, the use of equations 5, 6 and

7 should be used to predict oxygen solubility in alkanolamine plants.

The importance of this is that oxygen solubility decreases with increasing temperature of the absorber (typical operating range of 120–180°F), but then any oxygen leaks beyond the absorber (cross exchanger, reboiler and stripper), where temperatures can reach up to about 260°F, oxygen solubility can increase. Predicting degradation of the alkanolamine due to oxygen can become very difficult, depending on where the oxygen is coming into contact with the alkanolamine in the plant.

It is noted here that oxygen solubility in water has been performed at extreme-

ly high oxygen partial pressures (Figure 4). Again, note that oxygen solubility has a minimum solubility at about 212°F, and then the oxygen solubility increases with increasing temperature.

The best fit equation was equation 8 (see panel below).

**Effect of salts on oxygen solubility**

Oxygen solubility measurements have been reported in over 70 aqueous electrolyte (salt) solutions (reference 1, p59). Salting out, or lowering of solubility due to the presence of salts is the general rule for oxygen, helium, argon, CO<sub>2</sub> and many other gases, although some exceptions are known (for example, see reference 2, pp416–419). As is seen in Figure 5, increasing NaCl concentration can have a dramatic effect on the lowering the oxygen solubility in water.

Although there is no literature on oxygen solubility in water with added CO<sub>2</sub> at temperatures from 80–250°F, high pressure work (1–5MPa) of oxygen solubility with NaHCO<sub>3</sub> in water at temperatures from 122–302°F does show that added NaHCO<sub>3</sub> does decrease oxygen solubility compared to water (Figure 6). Again, it is seen that oxygen solubility decreases up to about 212°F, and then increases above 212°F to 302°F. It is noted that these studies also showed that added 0.01M NaOH or 0.1M NaOH also lowered the oxygen solubility in water.

**Conclusion**

The solubility of oxygen in water and various alkanolamine/water mixtures at temperatures from 60–180°F using a

Comparisons				
Comparison of ppm dissolved oxygen at 101.325kPa and 20.95% oxygen for water vs duplicate runs of 30% DEA in water, using dissolved oxygen probe				
Temp °C	Temp °F	100% DI H <sub>2</sub> O*	30% DEA (run 1)	30% DEA (run 2)
15.5	60	9.98	9.76	9.67
20	68	9.23	8.90	8.82
25	77	8.37	8.31	8.22
30	86	7.65	7.59	7.61
35	95	7.24	7.14	7.13
40	104	6.68	6.65	6.80
45	113	6.20	6.22	6.47
50	122	5.86	5.87	6.11
55	131	5.65	5.42	5.77
60	140	5.47	4.86	5.39
65	149	5.34	4.48	4.98
70	158	5.14	4.23	4.55
75	167	5.16	3.89	4.16
80	176	5.08	3.91	3.86
82	180	5.01	3.58	3.78

\*Measured with dissolved oxygen probe (this work)

Table 4

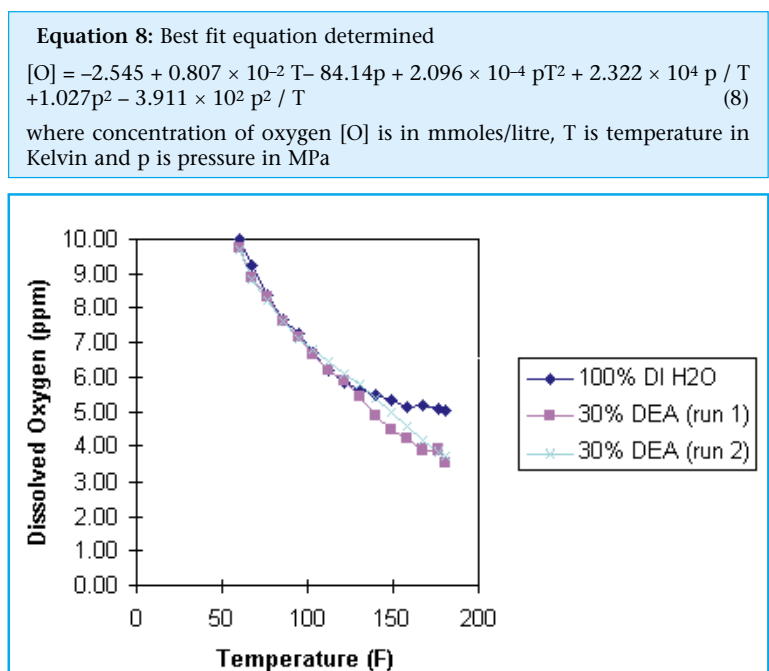


Figure 2 Comparison of ppm dissolved oxygen at 101.325kPa and 20.95% oxygen for water vs duplicate runs of 30% DEA in water, using dissolved oxygen probe

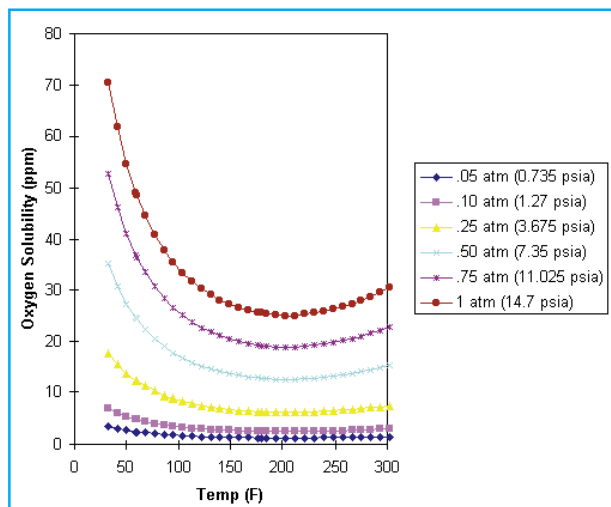


Figure 3 Solubility of oxygen in water at various partial pressures of oxygen

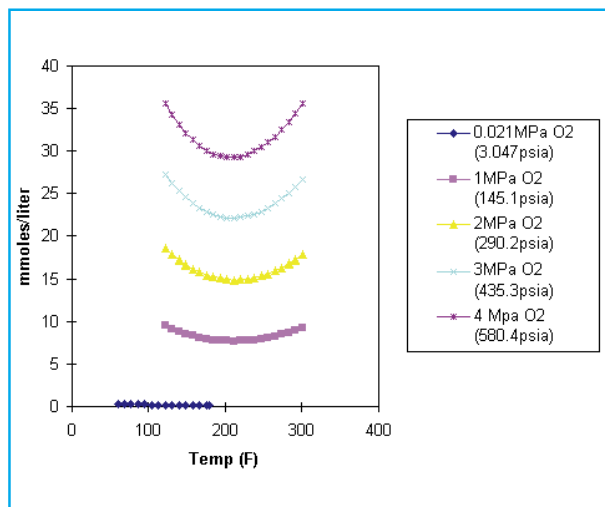


Figure 4 Solubility of oxygen at 1–4MPa partial pressure of oxygen compared to 0.021MPa (3.047psia; this work)

Mettler dissolved oxygen probe is reported. The alkanolamine/water mixtures chosen in this study are the most common generic solvents used in the gas treating industry to remove acid gases (CO<sub>2</sub> and H<sub>2</sub>S) from natural gas and synthesis gas.

It was found that the solubility of oxygen for all the alkanolamine/water mixture except the 30 per cent DEA were very similar to the oxygen solubility in water. In general, the oxygen solubility is about 10ppm at 60°F, and decreases to about 5ppm at 180°F. Duplicate runs of 30 per cent DEA showed similar solubility up to about 113°F, but then decreased to 3.6ppm at 180°F.

Literature reports show that the oxygen solubility increases with temperature starting at about 212°F. This suggests that the solubility of oxygen decreases with increasing absorber temperature (typical operating range of 120–180°F), but when any oxygen leaks

beyond the absorber (where temperatures can reach up to about 260°F) occur, oxygen solubility can increase.

Although no literature reports were found on the effect that CO<sub>2</sub> has on oxygen solubility, it is generally known that added salts generally results in a salting out effect (lowering of oxygen solubility). High pressure work using NaHCO<sub>3</sub> and NaOH does show the expected lowering of oxygen solubility (compared to water alone) up to about 212°F, and then an increase in oxygen solubility about 212°F.

This suggests that customers who maintain higher acid gas (CO<sub>2</sub> and H<sub>2</sub>S) loadings or salt concentrations (acetates, formates, chlorides etc) may minimise the effects of oxygen degradation on their amine.

This data will help quantitate and predict the effect that oxygen has on the degradation of alkanolamines to form heat stable salts in customer gas plants.

**Danny D Daniels** is a research technologist with The Dow Chemical Company, Freeport, Texas, USA. He holds a BS degree from Angelo State University in San Angelo, Texas.

**Peter C Rooney** is a research leader with the Gas/Spec Technology Group. He has a PhD degree in chemistry from the University of Texas at Arlington.

**Acknowledgement**

The authors gratefully acknowledge the many helpful discussions with Carolyn Buenger and Jenny Seagraves of GAS/SPEC TS&D.

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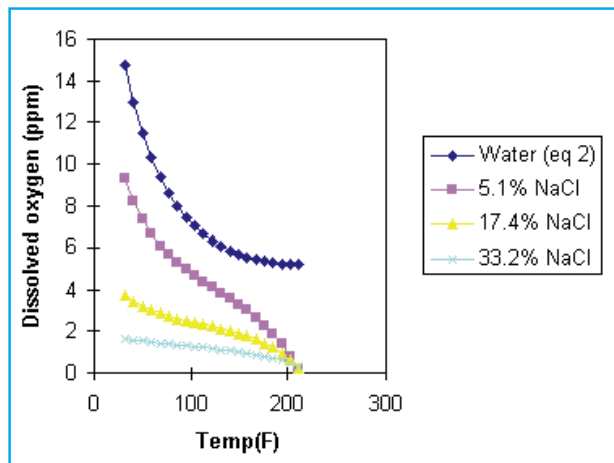


Figure 5 Effect of added NaCl on oxygen solubility of water

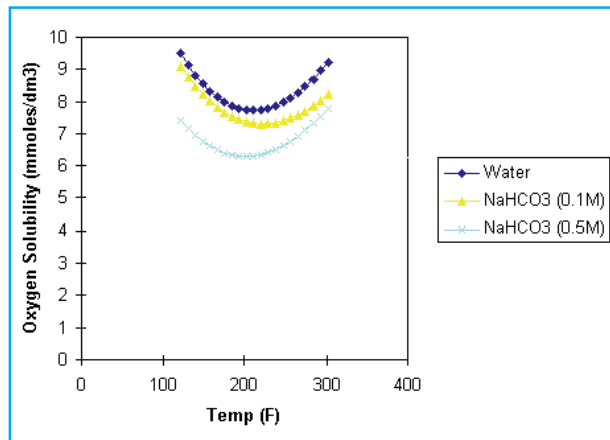


Figure 6 Effect of added NaHCO<sub>3</sub> on oxygen solubility in water at 1MPa

# INEOS

INEOS LLC  
Head Office

2925 Briarpark Drive, Suite 870, Houston, TX 77042  
713.243.6200 main 866.865.4747 customer service

[www.ineosllc.com](http://www.ineosllc.com)



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