

Solubility of oxygen in the Dead Sea brine

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Abstract

The solubility of the O₂ in the Dead Sea brine was determined over the temperature range 5 °C–50 °C using a modified Winkler titration, volumetric analysis, and a polarographic sensor. The solubility at room temperature and 1 atmosphere pressure was *ca.* 1 mg l⁻¹, and the temperature coefficient 0.006 mg l⁻¹ °C⁻¹. The data are nearly consistent with sea water solubility extrapolated to Dead Sea brine salinity.

Introduction

Dissolved oxygen (DO) concentration is associated with a multitude of chemical and biological processes. Hence DO analysis in saline lakes, such as the Dead Sea, can help to better characterize and understand the chemistry and the biology of the lakes. Furthermore, DO concentration can be used as a tracer to follow water masses and to better understand mixing and circulation (Craig, 1971; Ben-Yaakov, 1972).

Theoretical calculation of oxygen solubility in hypersaline solutions such as the Dead Sea waters (DSW) are presently difficult due to the uncertainty in exact formulation of all the interactions in mixed electrolytes of high ionic strength. Previous attempts to describe oxygen solubility in seawater (Green & Carrit, 1967; Weiss, 1970) applied experimental equations similar to the Setschenow exponential relationship (Harned & Owen, 1958) or a polynomial expansion (Weiss, 1970). It is therefore evident that

a critical examination of oxygen solubility in DSW must include a careful study to determine the solubility experimentally.

The objectives of the present research are to determine oxygen solubility in DSW and to evaluate the feasibility of using different analytical methods for determining the concentration of dissolved oxygen in this brine. The study used three analytical approaches; a modified Winkler titration (APHA, 1971); membrane covered dissolved oxygen electrode (Clark *et al.*, 1953; Ben-Yaakov, 1979, 1981); and gas stripping method.

Material and methods

The salinity of the Dead Sea water used during experiments was 280‰ (280 g kg⁻¹ or 345 gr l⁻¹) and the chemical composition: Cl⁻ 190, Ca²⁺ 14, Mg²⁺ 32.5, Na⁺ 33.3, K⁺ 7, Br⁻ 4 and SO₄²⁻ 0.35 gr kg⁻¹. Such DSW are about saturation with respect to gypsum.

Winkler titration

The Winkler or modified Winkler titration is widely used for determining dissolved oxygen concentration in natural and waste waters (APHA, 1971; Strickland & Parsons, 1972). The Winkler method is carried out in two steps: first, O_2 is reduced by oxidation of Mn^{2+} , and second the oxidized manganese is reduced as it oxidizes iodide to iodine. The iodine is then back titrated by thiosulfate using starch for end point detection. In order to ensure that the reactions be completed at a sufficient rate, the first reaction must, in DSW (Nishri, 1984), occur at relatively high pH whereas the second reaction must occur at low pH. These requirements are difficult to meet in DSW due to composition and high ionic strength. For example, attempts to raise the pH above *ca.* pH 8 by adding base is futile because of massive precipitation of Mg-hydroxides, which entrap dissolved oxygen. Another difficulty that might be encountered is precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) which will be formed if manganous sulfate is used for the first Winkler reagent and when acidifying the solution by H_2SO_4 to oxidize the iodide. To reduce these problems a modified procedure was applied to DSW. It has precipitation of *ca.* $\pm 2.5\%$ at $1 \text{ mg } O_2 \text{ l}^{-1}$.

The following procedure was used during Winkler titration of DSW:

1. 1 ml of reagent 1 ($MnCl_2$ 3 M) was added into a *ca.* 300 ml BOD bottle so that the initial Mn^{2+} was about 500 mg l^{-1} . This was followed by stirring for 2–3 sec.
2. 1 ml of reagent 2 (Strickland & Parsons, 1972) was introduced at the bottom of the bottle, the stopper replaced and the solution stirred for 5–10 min. If O_2 was present in a level more than 0.2 ml l^{-1} , the solution turns to a pale yellow color.
3. 1 ml of concentrated H_2SO_4 was added, the stopper replaced and the solution stirred for 2–3 min. The solid suspended is gypsum.
4. 10 ml were drawn from the top of the bottle and discarded. 2 ml of starch solution were then added and stirred for a few seconds.
5. Titration was carried out with thiosulfate (0.02

or 0.025 N) into the continuously stirred BOD bottle.

Membrane covered electrode

The Clark type (Clark *et al.*, 1953) membrane covered polarographic electrode is an electrochemical pO_2 sensor in which O_2 is reduced cathodically on the surface of a noble metal. The resulting electrical current is proportional to the rate at which O_2 is reaching the surface of the cathode. The current is thus a measure of the chemical potential (i.e. pO_2) driving the diffusion of O_2 across an inert membrane which separates the sample from the internal electrolyte of the sensor. Hence, this DO electrode can measure DO concentration only if the relationship between pO_2 and concentration (i.e. O_2 solubility) is known or if calibrated against an independent analytical method. Difficulties may arise when Clark electrodes are applied to DSW. Considerable diffusion of water vapor, due to large differences in the partial pressure of water, across the electrode membrane, may take place. Due to the high viscosity of DSW, adequate stirring could also be a problem.

The performance of a polarographic sensor was studied by comparing its response against the Winkler titration. The sensor used was similar to that described by Ben-Yaakov (1979); it has a gold cathode and a Ag/AgCl anode, a $1 \times 10^{-3} \text{ m}$ thick Teflon membrane and a 3 M KCl filling solution. A two membrane, flow-insensitive construction (Ben-Yaakov & Ruth, 1980), was also tested but later abandoned because it was less stable than the one membrane sensor.

The temperature sensitivity of the polarographic sensor was tested by monitoring the response of the electrode in DSW which was left to equilibrate with air at various temperatures.

Intercalibration between the Winkler titration and the membrane covered sensor was performed on air saturated samples through which nitrogen gas was bubbled for a few seconds to drive off some of the oxygen.

Gas stripping

A gas stripping method was employed using a special vacuum line on a DSW sample and transferring the released gas to a manometer via a toepler pump. Water vapor was trapped by freezing it with a mixture of dry ice and acetone.

Results and discussion

The solubility of O₂ in DSW was determined on temperature-controlled samples which were left, gently stirring, for 24 hours to equilibrate with air. The results obtained for the Winkler titration procedure are shown in Table 1, both in mg l⁻¹ and ml l⁻¹ units.

Cross calibration results between the Winkler titration and the gas stripping method are given in Table 2. It is apparent that the methods are consistent to within 10% when DSW solutions supersaturated with oxygen are used. The gas stripping method did not yield consistent results with an air saturated solution (in which nitrogen was present) for unexplained reasons. The fact that the precision of the Winkler titration was better than $\pm 2.5\%$ (Table 1) seems to indicate that the rather poor intercalibration results (Table 2) are mainly due to the lower precision of the gas stripping method.

The response of the DO electrode (Fig. 1) was found to correlate well ($r^2 = 0.97$) with that of the modified Winkler titration.

Table 2. Intercalibration of modified Winkler titration and gas stripping analysis, determined in DSW solutions in which pure oxygen gas was bubbled for different periods.

Sample No.	Stripping O ₂ ml l ⁻¹	Winkler O ₂ ml l ⁻¹	Deviation %
A	3.67	3.72	1.4
B	5.44	5.21	-4.2
D	4.06	3.62	-10.8
G	3.60	3.30	-8.3

The temperature sensitivity of the DO electrode (Fig. 2) follows the behaviour found in more diluted solutions, which is attributed to the temperature dependence of the O₂ diffusivity through

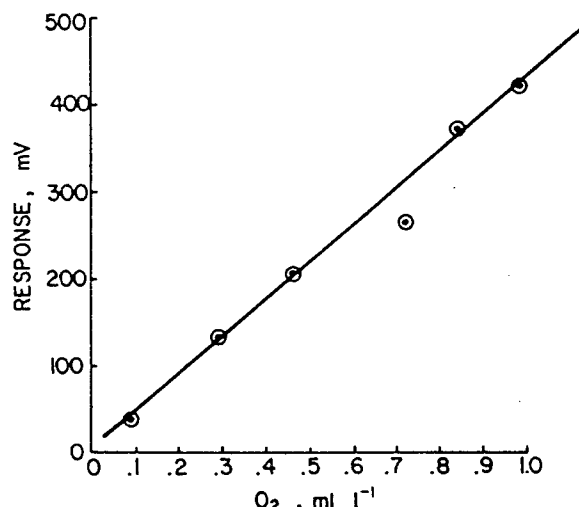


Fig. 1

Table 1. Dissolved oxygen concentrations in air saturated DSW as determined by the modified Winkler titration at an average barometric pressure of 0.99 atmospheres.

Temperature °C	Number of samples	Dissolved oxygen	
		ml l ⁻¹ *	mg l ⁻¹
4	10	1.105(±0.01)	1.65
25	10	0.981(±0.006)	1.45
46	5	0.788(±0.012)	1.15
47	6	0.798(±0.0078)	1.15
51	5	0.778(±0.01)	1.16

* Numbers in parenthesis are standard deviations.

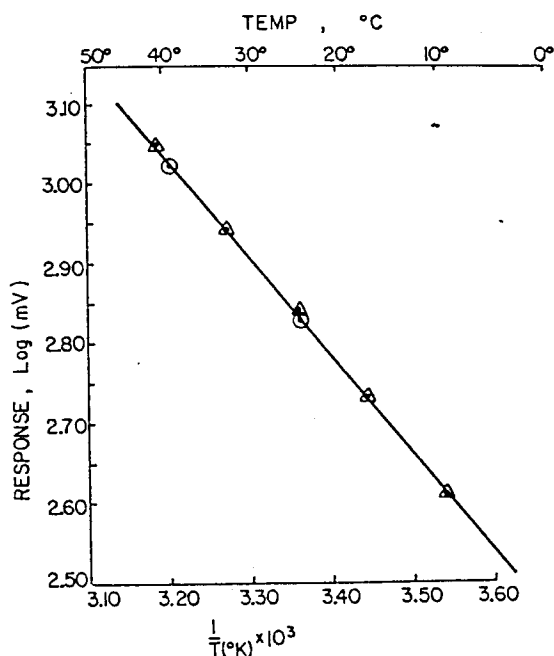


Fig. 2

plastic membranes (Ben-Yaakov, 1981). Although the response of the polarographic DO sensor appears normal, its application in routine analyses of DSW was difficult because of instability and apparent poisoning of the cathode surface. The useable lifetime of an electrode was only a few hours. Thereafter its response would drop dramatically and calibration would then be impossible. Rejuvenation was possible by polishing the sur-

face of the cathode and by replacing both the membrane and the inner electrolyte.

We suggest that two processes affect the response of the electrode. Water is probably lost from the thin electrolyte film which is normally present between cathode and the overlying membrane. This loss is driven by the difference in water vapor pressure between the inner 3 M KCl solution and the high ionic strength DSW. Diffusion through the membrane would deplete the water from the thin electrolyte layer to the point of KCl precipitation. Another interference is likely the poisoning of the cathode surface as DSW penetrates the membrane via pinholes or imperfect seals.

The concentration of dissolved O₂ in air saturated DSW is low and the temperature effect on the solubility is extremely small (Fig. 3), i.e. *ca.* 0.006 ml l⁻¹ °C⁻¹. In seawater the temperature effect is about 0.1 ml l⁻¹ °C⁻¹. However this is not expected if one extrapolates O₂ solubilities to DSW concentration by the experimental equation derived by Weiss (1970) for seawater:

$$\ln C = A_1 + A_2 (100/T) + A_3 (\ln(T/100)) + A_4 (T/100) + S\%_0 B_1 + B_2 (t/100) + B_3 (T/100)^2$$

where C is the solubility either in ml (STP) l⁻¹ kg⁻¹ in air saturated seawater at one atmosphere, and the A's and the B's are constants, T is the

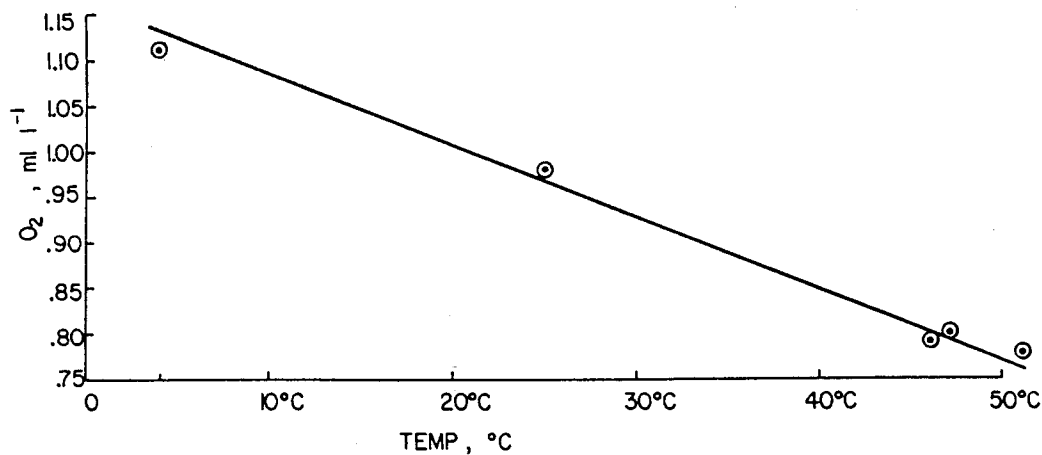


Fig. 3

absolute temperature and $S_{\text{‰}}$ is the salinity. Oxygen solubility in DSW is consistent with the extrapolated solubility as calculated from the above equation (Fig. 4).

Although the general behaviour of O_2 solubility at DSW salinities is predictable from the experimental equation, there is a large deviation between the extrapolated and measured values. This is not surprising considering the large difference in ionic composition between seawater and DSW.

Slightly higher (about 5%) oxygen saturation values were recently obtained in a series of experiments conducted by Shatkey & Gat (pers. commun.).

Weiss & Price (in litt.) have calculated a predicted value for solubility of oxygen in DSW by using an average of a Bunsen coefficient that was measured for argon and helium in diluted DSW. Their value of oxygen saturation (at $P = 1$ atm. $T = 25$ °C) is about 6.8% higher than our measurement.

For a single temperature, the experimental equation of Weiss (1970) reduces to the form

$$\ln C = A + S B,$$

or:

$$C = \exp A + S_{\text{‰}} B = C_0 \exp S_{\text{‰}} B$$

where A and B and C_0 are temperature-independent constants. The function is nonlinear, imply-

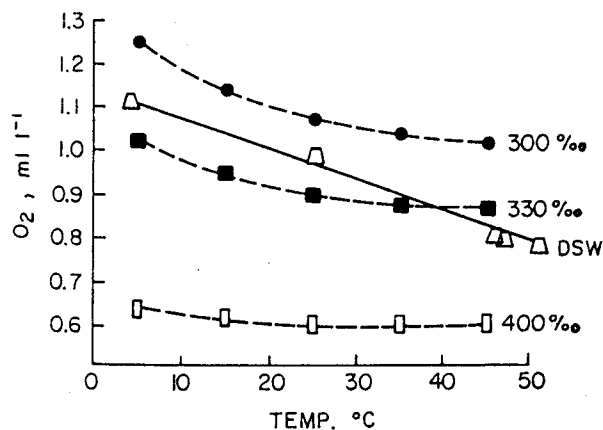


Fig. 4

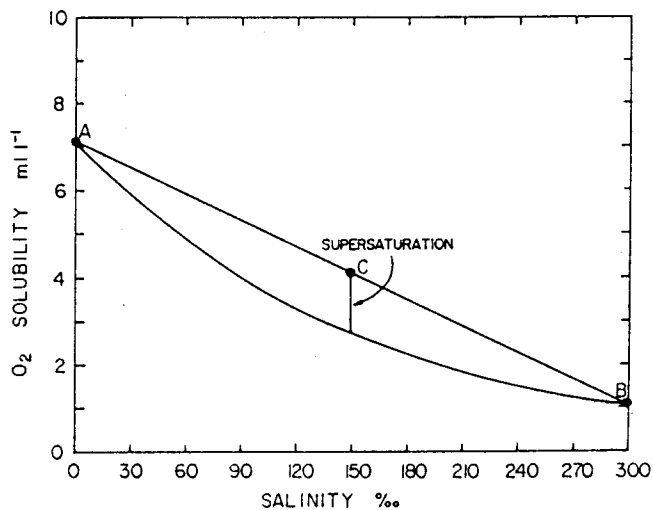


Fig. 5

ing that a mixture of two air-saturated brines will not be in equilibrium with atmospheric pO_2 . This behaviour is depicted in Fig. 5, from which the degree of supersaturation of mixtures can be deduced. For example a 1 : 1 mixture of air-satu-

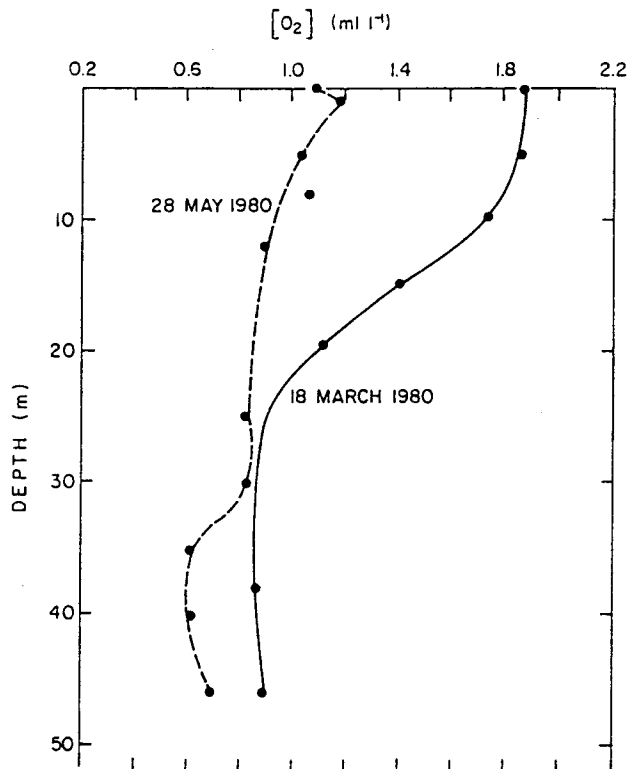


Fig. 6

rated fresh water and air-saturated DSW will be 30% supersaturated with respect to atmospheric pO_2 (Fig. 5). This conclusion has an important implication because it suggests that O_2 supersaturation will arise when O_2 rich rain waters are mixed into DSW. This mechanism is evidently operational in the Dead Sea which receives considerable amounts of flood water during winter. The O_2 profiles taken in a three month interval (Fig. 6) reveal a loss of O_2 to the atmosphere.

The oxygen concentration in the upper water layer measured on the 28 May 1980 is about 1.1 ml l^{-1} . This figure is about 10% more than expected from our solubility measurements at similar temperatures but at 1 atm pressure. If biological effects are negligible then part of the difference may be explained by the mean surface barometric pressure prevailing at the Dead Sea surface, of about 1.048 atm.

Conclusions

1. The modified Winkler titration procedure is shown to be a reliable technique for measuring DO concentration in the highly saline DSW.
2. As yet, the Clark type polarographic electrode is of value only for short duration DO measurements in DSW; its application for routine analysis is difficult.
3. The solubility of O_2 in DSW (at 25°C) is lower, by about 20%, than the extrapolated solubility of a 280 salinity solution, according to Weiss's (1970) experimental equation for much fresher solutions.
4. The temperature coefficient of solubility in DSW is *ca.* $0.006 \text{ mg l}^{-1} \text{ }^\circ\text{C}^{-1}$, and is, as expected from Weiss's equation, much smaller than that of fresher solutions.

5. As O_2 solubility is non-linear dependent on salinity, mixtures of air saturated brines of different salinity may yield a brine which is supersaturated with respect to atmospheric O_2 . This phenomenon evidently occurs in the Dead Sea system.

References

- American Public Health Association, American Water Works Association & Water Pollution Control Federation, 1985. Standard methods for the examination of water and wastewater. 16th ed. APHA, AWWA, WPCF, Wash. D.C., 1268 pp.
- Ben-Yaakov, S., 1979. A portable dissolved oxygen analyzer for the fish pond industry. *Bamidgeh* 31: 69-77.
- Ben-Yaakov, S., 1981. Electrochemical instrumentation. In: Whitfield, D. & Janger, D. (eds.), *Marine Electrochemistry*. John Wiley, New York, 99-122.
- Ben-Yaakov, S. & E. Ruth, 1980. A method for reducing the sensitivity of a polarographic dissolved oxygen sensor. *Talanta* 27: 391-395.
- Clark, L. C. Jr., R. Wolf, D. Granger & Z. Taylor, 1953. Continuous recording of blood oxygen by polarography. *J. Appl. Physiol.* 6: 189-199.
- Craigh, H., 1971. The deep metabolism: oxygen consumption in abyssal ocean waters. *J. Geophys. Res.* 76: 5978-086.
- Green, E. J. & D. E. Carrit, 1967. Oxygen solubility in sea water: Thermodynamic influence of sea salt. *Science* 157: 191-193.
- Harned, H. S. & B. B. Owen, 1958. *The physical chemistry of electrolytic solution*. Reinhold Brook Corp. New York.
- Nishri, A., 1984. The geochemistry of manganese in the Dead Sea. *Earth Planet. Sci. Lett.* 718: 415-426.
- Strickland, J. D. H. & T. R. Parsons, 1972. *Practical Handbook of seawater analysis*. Bull. Fish. Res. Bd Can. 167. 310 pp.
- Weiss, R. F., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep Sea Res.* 17: 712-735.
- Weiss, R. F. & B. A. Price (in litt.). *Dead Sea gas solubilities* (Manuscript 9 pp, 2 tables).