

# Bunsen Coefficient for Oxygen in Marine Oils at Various Temperatures Determined by an Exponential Dilution Method with a Polarographic Oxygen Electrode

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## ABSTRACT

A polarographic oxygen electrode has been applied to an exponential dilution method for the determination of the solubility of oxygen in oils. Results are compared with other chemical and physical methods for herring and olive oils and the same oils subjected to partial oxidation. The Bunsen coefficients for oxygen in nine marine oils have been determined by this procedure between 20 and 80 C, with a relative standard deviation of  $\pm 7\%$  or less. The densities and viscosities of these oils have been measured for the same temperature range. In general, the Bunsen coefficient for oxygen in marine oils increases with an increase in temperature between 20 and 60 C, but then rapidly decreases between 60 and 80 C to a value lower than that for room temperature. It appears that autoxidation should not be the major cause of this effect, as the measurement rate was relatively rapid. Some tentative correlations between the solubility of oxygen in marine oils and the fatty acid composition, iodine value, density and viscosity are discussed briefly.

## INTRODUCTION

The solubilities of gases in liquids, which were reviewed in detail by Battino and Clever (1) in 1966, have become increasingly more important for the theoretical understanding of both the liquid state and solution and for practical application with various materials such as fats and oils. Dissolved oxygen, which leads to autoxidation and rancidity and thus affects the palatability and nutritive value, is a major concern of the food and edible oil industries (2). Since most marine oils contain a relatively high proportion of polyunsaturated fatty compounds (3), the sorption of oxygen from air to these oils is often an important cause of deteriorations of fish and related products (3-5).

In addition to recent chemical methodology (6,7), the improvement of instrumentation for the determination of oxygen solubility in liquid samples has involved the use of gas chromatography (8), membrane electrodes (9,10) and polarographic analysis (11,12). However the application of these techniques to viscous peroxidized or polymerized oil samples gives rise to considerable technical difficulties. Comparisons between the determinations of the solubility of oxygen by polarographic and the classical physical and chemical methods have been reported from other laboratories (13,14). The polarographic oxygen sensor, which has been generally accepted for water analysis, can also be used, with some specific modifications, for the determination of oxygen content of oils. An exponential dilution procedure

for the determination of oxygen in oils based on a silver-gold oxygen electrode has been tested by Aho and Wahlroos (15). A combined polarographic and exponential dilution method for the determination of the solubility of oxygen in oils by means of a newly designed sample vessel and measuring apparatus is described. Comparisons are reported with the viscosity and density for nine marine oils in the temperature range of 20-80 C.

## EXPERIMENTAL PROCEDURES

### Samples

Nine marine oils and an olive oil sample were used for this investigation (Table I). Oils from whole herring (*Clupea harengus*), cod (*Gadus morhua*) livers, sperm whale (*Physeter catodon*) blubber (including wax esters) and harp seal (*Phoca groenlandica*) blubber were obtained from local commercial reduction plants in Nova Scotia. Oils from whole capelin (*Mallotus villosus*), redfish viscera and scrap (*Sebastes marinus*), flounder viscera and scrap (*Pseudopleuronectes americanus*), mackerel (*Scomber scombrus*) bodies, and whole barracudina (*Paralepis rissoi krøyeri*; see *JAACS* 49:378 [1972] including wax esters) were produced in a pilot scale reduction plant at the Vancouver Laboratory of the Fisheries Research Board of Canada. No antioxidants were added to any of these samples. All oils were kept under nitrogen in cold storage (3 C), except when the experiment was in progress. Olive oil (Italian origin) was purchased from a local retail store. Analytical data listed in Table I include typical major fatty acid unsaturated components summarized from previous work on these oils. Partially oxidized herring and olive oils were prepared by bubbling air through a capillary tube into the oils at 60 C for several hours or overnight. The peroxide values of these partially oxidized oils were determined just before the exponential dilution measurement of dissolved oxygen in the sample was started and while they were still saturated with air.

### Apparatus

The glass vessel (volume empty ca. 180 ml) was designed and made as shown in Figure 1. A Haake FJ Constant Temperature Circulator was used to maintain the oil sample in the vessel at temperatures found by thermometer to be constant within 0.05 C. A magnetic stirring bar (8 x 50 mm) sealed in Teflon was placed in the sample vessel for stirring at 120 rpm with a speed-regulated Magnestir (Labline, Inc.). The total effective volume (170.2 $\pm$ 0.5 ml) was determined carefully by weighing water in the fully filled vessel after the stirring bar and the polarographic oxygen sensor (passed through a rubber stopper) had been placed in position in the vessel. The vessel constant (a ratio

TABLE I  
Analytical Data and Typical Major Fatty Acid Compositions of Nine Experimental Marine Oils

Oil	Triglyceride oils						Wax ester oils <sup>a</sup>		
	Redfish	Capelin	Herring	Mackerel	Harp seal	Flounder	Cod liver	Sperm whale	Barracudina
Iodine value (Wijs)	125	133	139	146	149	150	165	85	125
Unsaponifiable matter, %	2.2	3.1	1.4	1.8	0.7	2.3	2.8	1.7	2.1
Free fatty acid as oleic, %	3.7	3.7	4.5	3.9	0.8	1.9	2.8	0.9	0.7
Peroxide value, meq/kg	6.4	11.8	2.0	8.1	0.5	1.8	2.1	0.8	0.6
Fatty acid wt% from									
b									
c									
d									
e									
f									
g									
h									
i									
j									
Σ Polyunsaturated	19.4	23.7	23.8	28.3	23.7	27.2	31.7	7.8 (tr) <sup>j</sup>	27.3 (tr)
22:6	3.3	8.2	5.3	11.0	6.7	4.6	12.5	2.2 (tr)	9.8 (tr)
20:5	7.3	8.3	8.5	7.3	7.5	12.3	11.3	1.7 (tr)	9.1 (tr)
22:5	tr	1.0	1.0	1.7	3.9	1.4	2.0	—	—
Σ Monounsaturated	63.9	56.0	54.1	45.6	60.8	51.3	47.8	76.3 (60.7)	52.4 (44.0)
16:1	13.3	12.1	8.5	6.2	18.0	12.5	11.6	25.4 (9.6)	13.4 (tr)
18:1	13.3	9.4	9.9	14.8	24.7	16.5	23.3	34.2 (44.9)	28.2 (29.6)
20:1	17.2	16.6	14.9	6.0	12.5	11.3	7.9	10.3 (5.0)	4.5 (8.4)
22:1	18.9	16.1	19.3	12.9	4.0	9.0	5.5	2.1 (tr)	4.5 (5.6)
Other relationships									
16:0	13.3	10.9	12.5	16.2	8.2	9.7	13.4	9.6 (24.9)	7.6 (42.4)
Σn:5+6/16:0	0.86	1.64	1.24	1.28	2.24	1.96	1.93	0.41	2.64
Σw3/Σw6	6.9	10.7	9.9	6.1	9.2	10.9	7.3	—	—

<sup>a</sup>Sperm whale body oil contains 79% wax esters and 21% triglycerides; barracudina oil contains 85% wax esters and 10% triglycerides. The data in the brackets are wt% of alcohols from wax esters.

<sup>b</sup>Ackman, R.G., and P.J. Ke, J. Fish. Res. Bd. Canada 25:1061 (1968).

<sup>c</sup>Ackman, R.G., et al., Ibid. 26:2037 (1969).

<sup>d</sup>Ackman, R.G., and C.A. Eaton, Ibid. 23:991 (1966).

<sup>e</sup>Ackman, R.G., and C.A. Eaton, Can. Inst. Food Technol. J. 4:169 (1971).

<sup>f</sup>Jangaard, P.M., and P.J. Ke, J. Fish. Res. Bd. Canada 25:2419 (1968).

<sup>g</sup>Jangaard, P.M., et al., Ibid. 24:613 (1967).

<sup>h</sup>Hansen, I.A., and C.C. Cheah, Comp. Biochem. Physiol. 31:757 (1969).

<sup>i</sup>Ackman, R.G., et al., JAOCS 49:378 (1972).

<sup>j</sup>tr = wt% less than 1%.

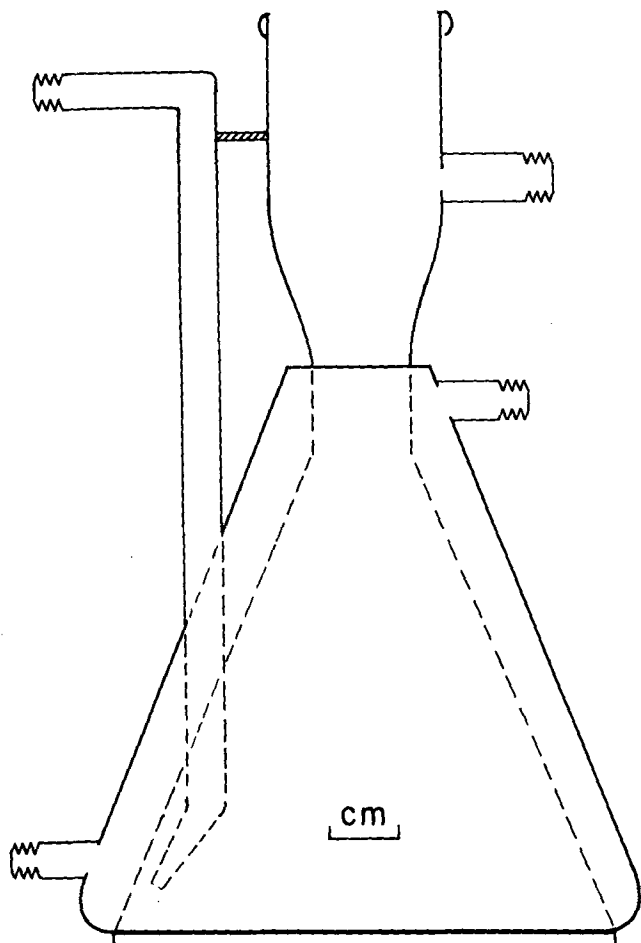


FIG. 1. Sample vessel.

$V_A/V_S$ , A = top air space, S = sample) could be determined and adjusted between 0.0704 and 0.0981, for weighed oil samples of 155-159 ml, with an error due to operating variations <2%.

The experimental assembly is shown in Figure 2. Some modifications were made from that of the previous study (15) in order to carry out the determination more reproducibly at higher temperature. Besides the constant temperature sample vessel, a glass, coiled-tube condenser (500 mm) hooked up with the circulator was employed to preheat helium gas before it was admitted to the sample vessel. A water jacket (room temperature) was used for the water-filled gas buret to minimize thermal variation during gas measurements. A Beckman 39550 polarographic oxygen sensor consisting of a rhodium cathode and silver anode, with a Teflon membrane to separate the electrolyte and sample, was used to determine the oxygen concentration in the sample vessel head space. The actual measurement was read from a Beckman Fieldlab Oxygen Analyzer.

#### Methods

Oil was degassed with a mechanical vacuum pump in a Battino flask (16) for 2 hr, using a dry ice-acetone trap between the flask and pump. The degassed oil (155-159 ml) was poured into the sample vessel and the weight of oil was measured to  $\pm 0.1$  g. The oil was saturated with air, while being brought to the desired constant temperature, by bubbling in breathing grade compressed air (at the experimental temperature) at a flow rate of 15 ml/min (with stirring) for ca. 2 hr. The oxygen analyzer was calibrated under the same condition as the determination before the air flow was discontinued. Stirring was continued for 2 min after the air flow was stopped to avoid supersaturation. Helium preheated to the oil temperature was introduced into the oil at a rate of 7-10 ml/min for the dilution

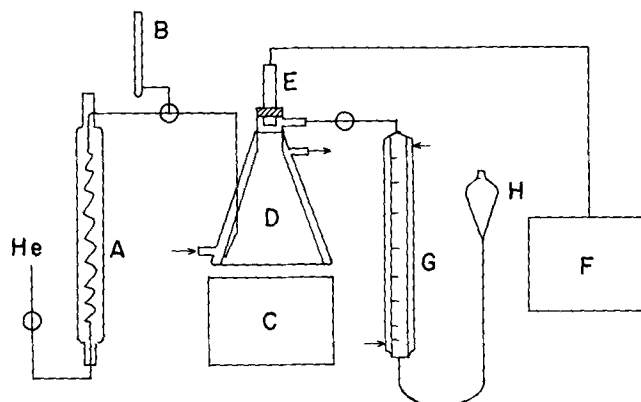


FIG. 2. Experimental arrangement for determination of Bunsen coefficient for oxygen in oil by polarographic and exponential dilution method. A. Pre-heater for helium; B. flow meter; C. magnetic stirrer; D. sample vessel; E. polarographic oxygen sensor; F. Beckman oxygen analyzer; G. gas buret; H. 150 ml separatory funnel for balancing buret.

determination of oxygen solubility. The measurement phase (80 ml helium passed through the oil sample) took ca. 10 min. The oxygen concentration was either read at regular intervals or read as each 10 ml of helium was collected in the gas buret. Temperature and barometric pressure corrections were applied subsequently. Very good plot linearity was obtained for  $\log C$  (oxygen concentration) vs.  $V_D$  (D=diluting gas, in this case helium), due both to its low density (15) and to its slight solubility in oils (17). The slope of the  $\log C$  vs.  $V_D$  curve could be measured for the range 10-70 ml helium with an error of <5%. For comparison, a chemical method (18) and a displacement method (14) were used with two oil samples before and after oxidation (Table II). Viscosities and densities were determined with Cannon-Fenske modified Ostwald viscometers and Gay-Lussac pycnometers at temperatures between 20 and 80 C. Chemical data were determined according to the AOCS official methods.

#### Calculation

On the basis of previous exponential dilution techniques (15,19), several equations have been derived and used to compute the oxygen solubilities. The Ostwald coefficient (L) is defined as the ratio of the volume of gas absorbed ( $V_g$ ) to the volume of absorbing liquid ( $V_S$ ), i.e.,  $L = V_g/V_S$ . When a volume of diluting gas ( $V_D$ ) is passed through the sample vessel, which contains the air saturated oil ( $V_S$ ), and a small volume of air ( $V_A$ ), a change of oxygen concentration before and after a dilution,  $C_{O1}$  and  $C_{O2}$ , can be expressed as:

$$C_{O2} = C_{O1} \exp \left[ \frac{-V_D}{V_A + LV_S} \right] \quad [I]$$

This can also be expressed by a logarithmic equation as:

$$\log C_{O2} = \left[ \frac{-0.434}{V_A + LV_S} \right] V_D + \log C_{O1} \quad [II]$$

When the slope (S) is determined graphically from the experimental curve of  $\log C$  vs.  $V_D$ , the Ostwald and Bunsen coefficients (L and  $\alpha$ ) can be calculated simply from the equations (III) and (IV), respectively:

$$L = \frac{0.434}{SV_S} \cdot \frac{V_A}{V_S} \quad [III]$$

$$\alpha = L \left[ \frac{273.2}{T} \right] \quad [IV]$$

TABLE II

Comparison of Bunsen Coefficients Determined for Oxygen by Various Methods in Olive and Herring Oils in Fresh and Partially Oxidized Forms

Oil	Temperature, C	Density, g/cc	Peroxide value, meq/kg	Bunsen coefficient $\alpha^a$			
				PED method <sup>b</sup>	Chemical method	Displacement method	Others
Olive	20	0.9235	0.9	0.102 ( $\pm 6\%$ )	0.109 ( $\pm 8\%$ )	0.098 ( $\pm 6\%$ )	0.116 (t=25.1 C, d=0.904) <sup>c</sup> 0.112 (t=25.3 C, d=0.912) <sup>d</sup>
	20	0.9235	41.5	0.106 ( $\pm 6\%$ )	0.150 ( $\pm 16\%$ )	0.107 ( $\pm 8\%$ )	
	40	0.9114	1.0	0.110 ( $\pm 5\%$ )	0.121 ( $\pm 10\%$ )	---	0.117 (t=35.1 C, d=0.899) <sup>c</sup> 0.119 (t=45.4 C, d=0.894) <sup>c</sup> 0.102 (t=38 C, d=0.912) <sup>e</sup>
	40	0.9114	63.8	0.113 ( $\pm 6\%$ )	0.192 ( $\pm 19\%$ )	---	
	20	0.9151	2.0	0.110 ( $\pm 6\%$ )	0.124 ( $\pm 11\%$ )	0.113 ( $\pm 8\%$ )	
	20	0.9151	21.4	0.108 ( $\pm 7\%$ )	0.149 ( $\pm 18\%$ )	0.119 ( $\pm 7\%$ )	
Herring	20	0.9151	79.5	0.113 ( $\pm 6\%$ )	0.214 (-)	---	
	20	0.9151	21.4	0.108 ( $\pm 7\%$ )	0.149 ( $\pm 18\%$ )	0.119 ( $\pm 7\%$ )	
	20	0.9151	79.5	0.113 ( $\pm 6\%$ )	0.214 (-)	---	
	40	0.9034	2.3	0.128 ( $\pm 5\%$ )	0.141 ( $\pm 9\%$ )	---	
	40	0.9034	84.0	0.122 ( $\pm 6\%$ )	0.289 (-)	---	
	40	0.9034	84.0	0.122 ( $\pm 6\%$ )	0.289 (-)	---	

<sup>a</sup>Percentage of relative error calculated from three determinations.

<sup>b</sup>PED method is an abbreviation for polarographic exponential dilution method.

<sup>c</sup>Data from Battino et al., JAOCS 45:830 (1968).

<sup>d</sup>Data from Davidson et al., Quart. J. Exp. Physiol. 37:91 (1952).

<sup>e</sup>Data from Vibrans, JAOCS 12:14 (1935).

where T is the absolute temperature during the measurement and all volumes are reduced to 760 mm pressure.

The solubilities of oxygen in fats or oils, which are usually presented in units of either weight (ppm) or volume (ml of oxygen at standard condition dissolved in 100 ml of oil), may be computed from the equations as:

$$(w/w) = \text{ppm} = 0.393 \frac{\alpha P_m}{d} \quad [V]$$

$$(v/v) = \frac{(\text{ml O}_2 \text{ at STP})}{100 \text{ ml oil}} = 0.0275 \alpha P_m \quad [VI]$$

where  $P_m$  and  $d$  denote the pressure in mm Hg and density of the oil in g/ml.

## RESULTS AND DISCUSSION

The influence of various factors on the sorption rate of oxygen in oil has been discussed previously (20). The experimental lack of reproducibility is probably due to complex interactions among diffusion, solubility, membrane permeability, slow approach to equilibrium and thermal effects.

The membrane-covered polarographic oxygen sensor operating in a gas environment allows sensitive measure-

ment of oxygen concentration without interference from peroxides, metals or the oil itself. However, as the sensor is covered with a thin Teflon membrane, stirring of the oil must be kept at a minimum of 100 rpm to prevent establishment of a concentration gradient in the gas space near the electrode. (With a 50 mm stirring bar in the vessel described, 120 rpm was found to be adequate as the standard for this study.) In the determination of the solubility of oxygen in oil by the exponential dilution method, Aho and Wahlroos (15) have observed that deviations were caused by insufficiently rapid diffusion in the gas phase. In the present study, most difficulties have been satisfactorily minimized with the new shape of the sample vessel and by optimizing operational details as described above.

In order to compare the accuracy of the polarographic exponential dilution technique with other procedures, a chemical method (18) and a physical displacement method (14) were also employed to estimate the Bunsen coefficient for oxygen in samples from the same lots of olive and herring oils. All experimental results are averaged for three determinations on each oil sample. Results determined by the three methods are compared in Table II. Since the polarographic sensor is not responsive to chemically reacted oxygen in the form of peroxides, epoxides, etc., an appreciable difference for the chemical method is observed in oxidized oils. This disadvantage of the chemical method, due to its lack of discrimination between physically

TABLE III

Bunsen Coefficients and Solubilities for Oxygen in Marine Oils at Temperatures between 20 and 80 C<sup>a</sup>

Temperature, C	$\alpha$				ppm, $\mu\text{g/g}$				ml O <sub>2</sub> (STP)/100 ml oil			
	20	40	60	80	20	40	60	80	20	40	60	80
Triglyceride oils												
Redfish oil	0.074	0.078	0.088	0.012	24.2	25.8	29.6	4.1	1.55	1.64	1.84	0.25
Capelin oil	0.060	0.081	0.103	0.025	19.5	26.6	34.4	8.5	1.25	1.68	2.14	0.52
Herring oil	0.110	0.128	0.135	0.076	35.8	42.2	45.2	25.8	2.29	2.26	2.81	1.58
Mackerel oil	0.042	0.078	0.086	0.011	13.6	25.6	28.7	3.7	0.87	1.62	1.79	0.23
Harp seal oil	0.090	0.108	0.114	0.030	29.1	35.7	37.9	10.1	1.87	2.26	2.37	0.62
Flounder oil	0.075	0.078	0.081	0.029	23.2	25.6	26.9	9.6	1.55	1.63	1.69	0.59
Cod liver oil <sup>b</sup>	0.124	0.146	0.130	0.018	39.9	47.6	43.0	6.0	2.58	3.04	2.70	0.37
Wax ester oils												
Sperm whale oil	0.109	0.125	0.117	0.070	37.0	43.1	40.9	24.9	2.27	2.60	2.46	1.45
Barracudina oil	0.092	0.095	0.080	0.058	30.4	32.1	27.5	20.2	1.91	1.98	1.67	1.21

<sup>a</sup>Data are average of three determinations with relative standard deviation of 7% or less.

<sup>b</sup>Relative error for cod liver error is ca. 9%.

TABLE IV  
Viscosities and Densities of Nine Marine Oils between 20 to 80 C

Oil	Density, g/cc				$\delta$ (Temperature coefficient of density), (g/cc °C) <sup>a</sup>	Viscosity (centipoise)			
	20	40	60	80		20	40	60	80
Triglyceride oils									
Redfish oil	0.9184	0.9061	0.8931	0.8814	4.63	68.73	31.78	17.41	10.81
Capelin oil	0.9163	0.9049	0.8920	0.8798	4.65	78.14	35.43	19.09	11.64
Herring oil	0.9151	0.9034	0.8904	0.8785	4.59	75.65	33.41	18.44	11.27
Mackerel oil	0.9192	0.9074	0.8952	0.8828	4.55	67.99	30.64	16.94	10.64
Harp seal oil	0.9220	0.9087	0.8970	0.8844	4.70	61.38	28.62	16.16	10.23
Flounder oil	0.9234	0.9115	0.8977	0.8853	4.71	65.30	30.08	16.68	10.60
Cod liver oil	0.9265	0.9139	0.9002	0.8896	4.62	59.95	28.72	16.23	10.28
Wax ester oils									
Sperm whale oil	0.8775	0.8639	0.8514	0.8378	4.96	33.98	17.10	10.01	6.49
Barracudina oil	0.8933	0.8812	0.8679	0.8553	4.79	31.79	17.42	10.42	6.96

<sup>a</sup>Temperature coefficient of density was experimentally determined and can be used to estimate the density at various temperature from the equation:  $d_t = d_{20} - \delta(t - 20)$ .

dissolved and chemically reacted oxygen, has been reiterated previously (11,15,20). The time consuming displacement procedure gave nearly the same results as the polarographic exponential dilution method, but gave a slightly larger deviation. In comparison with the previous data, the Bunsen coefficient for oxygen in olive oil, determined by the present method, is generally smaller. This may be due to the variations in oil quality or composition, since the densities reported are not uniform. It can therefore be concluded that the exponential dilution method combined with a polarographic oxygen sensor can be usefully employed for the determination of dissolved oxygen in oil samples. Even for those samples with a high content of chemically reacted oxygen, the relative deviation was still less than  $\pm 7\%$ .

In Table III the Bunsen coefficients, weight and volume solubilities for oxygen in nine marine oils are presented for the temperature range between 20 and 80 C. The respective Bunsen coefficients for the different oils at various temperatures have been plotted in Figure 3. The Bunsen coefficients of six triglyceride marine oils (curves A-F) increase with increasing temperature up to 60 C, and then drop rapidly to values much lower than that at room temperature when the temperature of measurement is raised to 80 C. Cod liver oil (curve G), which has the highest iodine value, reaches a maximum Bunsen coefficient value at 40 C, decreases slightly to 60 C and finally drops to a value lower than the other five triglyceride oils at 80 C. Sperm whale oil and barracudina oil (curves H and I), which contain wax esters (21,23), behave slightly differently from the triglyceride oils. Their coefficients also increase from 20 to 40 C, but then gently decrease over the temperature range between 40 and 80 C. Oxygen in water decreases in solubility as temperature increases (1).

We are unaware of Bunsen coefficient data for oxygen in marine oils, although it is known to be important (20,22). Bailey has summarized some solubilities of air, oxygen, nitrogen, hydrogen and carbon dioxide in lard and cottonseed oil (24). The increases in solubilities with temperature increasing from 30 to 40 C have been noticed, but as there are only two figures available for these relatively lower temperatures no significant conclusion can be drawn. The oxygen content of butter oil at 40 and 60 C has been estimated by a physical method (25), but the small difference of the results is within the error limit and cannot indicate a thermal effect for the solubility. The solubility of oxygen and other gases in soybean oil at temperatures from 30 to 70 C has been investigated (26). This study concluded that the solubility of the most gases in soybean oil follows Henry's Law; but the solubility of oxygen at 50 C was the same as at 30 C, while at 70 C it was twice as large as at 30 C. Unfortunately, no determination has been made at a

temperature higher than 70 C. In general, our results (Table III) are in agreement with the rather limited previous findings. However the considerable reduction in the solubility of oxygen in marine oils between 60 and 80 C cannot be interpreted without further research. It is possible that autoxidation of lipids at higher temperatures could affect the present determination. However autoxidation in oils, which is relatively slow (23,27,28), should not reduce the quantity of dissolved oxygen during the measuring period of less than 10 min. Therefore there must be other physical or chemical factors to control this change for marine oils between 60 and 80 C. As the physical properties of marine oils at higher temperatures have not been studied recently, we have also determined the densities and viscosities of the nine marine oils for the temperature range of 20-80 C (Table IV). For the seven triglyceride marine oils, the densities exhibit a substantially linear variation with the temperature, decreasing ca.  $4.6 \times 10^{-4}$  for each increment in temperature of 1 C. At a given temperature, the difference between maximum and minimum density for the triglyceride marine oils studied in this report is less than 1.5%. The temperature coefficients of density (Table IV) are comparable with some previous

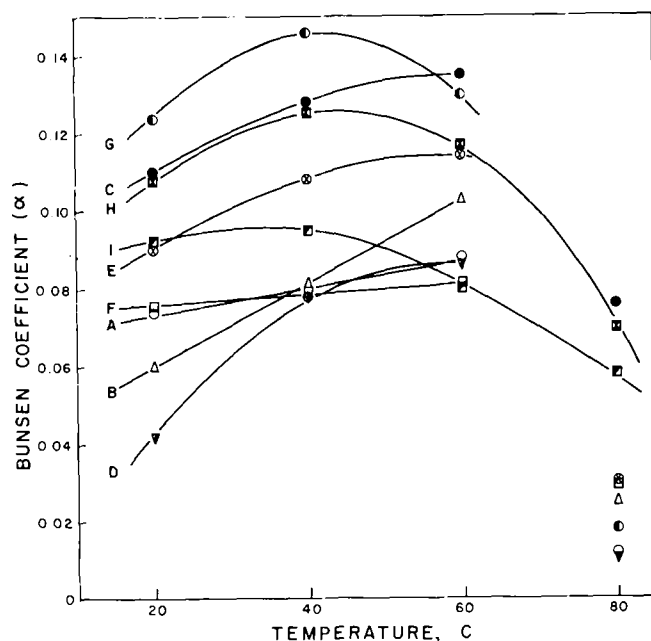


FIG. 3. Variation of Bunsen coefficients for nine marine oils at various temperatures. A. (○) Redfish oil; B. (△) capelin oil; C. (●) herring oil; D. (▽) mackerel oil; E. (⊗) harp seal oil; F. (□) flounder oil; G. (●) cod liver oil; H. (■) sperm whale oil; I. (■) barracudina oil.

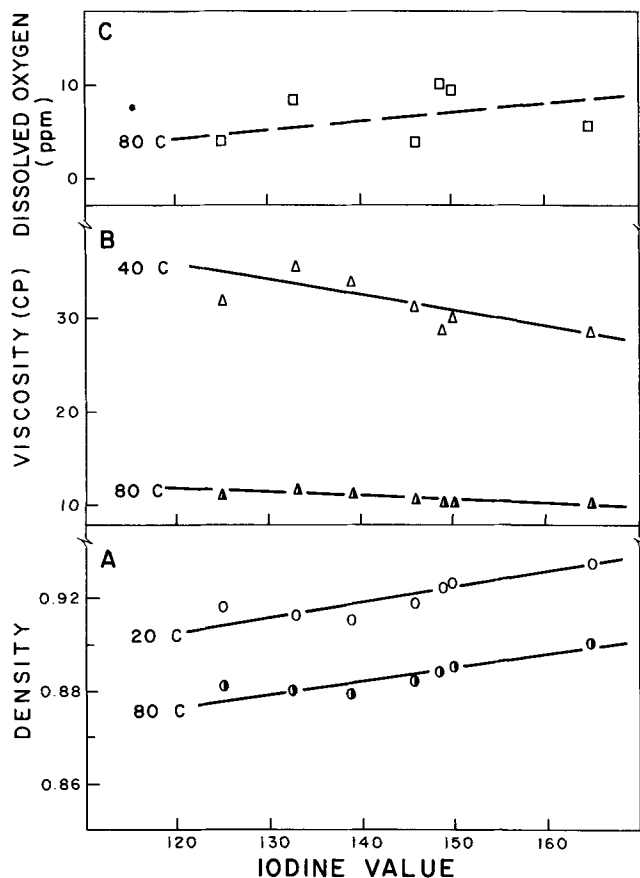


FIG. 4. Variation of dissolved oxygen, viscosity and density with iodine value in triglyceride marine oils.

reports (24,29). For harp seal oil our finding of ( $\delta = 4.70 \times 10^{-4} \text{ g/cc } ^\circ\text{C}$ ) is much lower than the result of  $6.77 \times 10^{-4}$ , which has been published recently for Caspian seal oil, although the iodine value of 187 for the latter is higher (30). In agreement with earlier investigations (31), an approximately linear relation between density and iodine value for seven triglyceride oils is obtained (Fig. 4A). In contrast to triglyceride oils, the densities of two wax ester marine oils are much less and have larger temperature

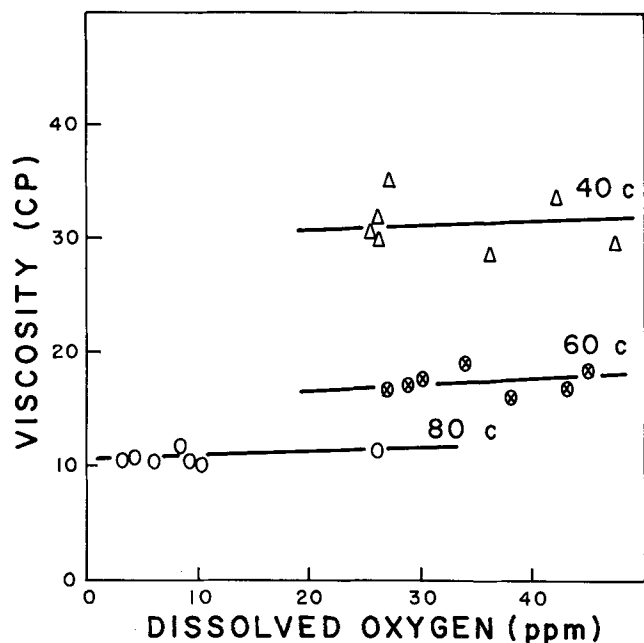


FIG. 5. Variation of dissolved oxygen with absolute viscosity in marine oils at various temperatures.

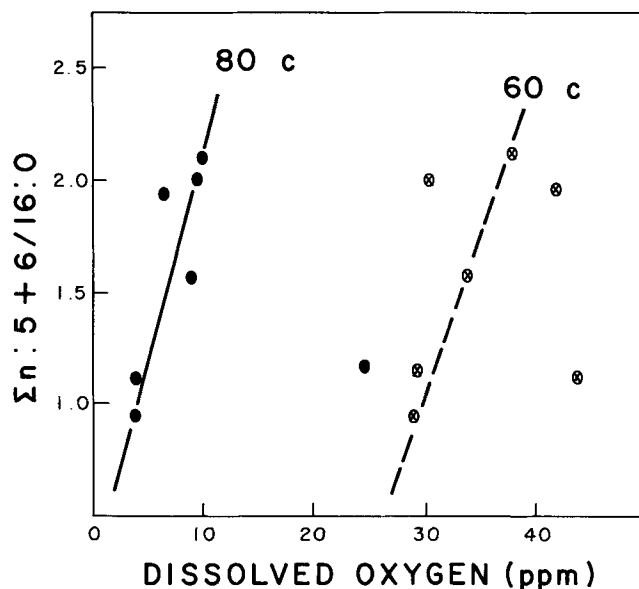


FIG. 6. Approximate correlation between the oxygen solubility and the fatty acid composition in marine oils.

coefficients. The relation between density and iodine value parallels but does not fit the same line as the triglyceride oils. Density does not show an irregular behavior at higher temperatures that can be linked to oxygen solubility.

The viscosity of triglyceride marine oils is about twice as high as the wax ester marine oils in the temperature range from 20 to 80 C. The reduction of viscosity is not proportional to the increase of temperature for both kinds of marine oils, and the temperature coefficient of viscosity is observed to be decreased at higher temperature ranges (Table IV). For the triglyceride oils, an approximate linear relation between viscosity and iodine value has been found (Fig. 4B), but owing to the small number of samples that have been investigated it is difficult to be more precise as to the validity of the relation.

In the higher temperature range a viscosity increase as a function of oxygen absorption has been reported for some mineral oils (32) and for water under high pressure (33). The same change of viscosity in soybean oil with various quantities of nitrogen at 30 C has also been reported (26). The slight increase of viscosity with the increase in oxygen dissolved in the different triglyceride oils detected in this investigation is shown in the plot of Figure 5 for three different temperatures.

A knowledge of the chemical nature and composition of fatty acids in marine oils is important in order to understand the physical and chemical properties of marine oils. However marine oils present unusual difficulties to the chemists because of the wide variety of species, seasonal variations in composition, the high proportion of polyunsaturated fatty acids (especially those with five or six double bonds), and various other factors such as phospholipid, hydrocarbon and sterol content. As indicated by recent papers (34,35) the solubility of oxygen in oils should be related to the distribution and structure of all of the fatty acids. However there is insufficient experimental evidence to indicate whether the variation could be correlated meaningfully with particular groups of acids, i.e., saturated, monounsaturated and polyunsaturated. Tentative correlations such as the higher dissolved oxygen with the increase of iodine value (Fig. 4C) and with  $\Sigma n:5 + 6/16:0$  (Fig. 6) suggest that such relationships are possible. A demonstration of the general validity of these relationships, and an explanation, requires a larger number of samples, uniform analytical determinations of fatty acid composition and probably a rigorous mathematical treatment.

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