• *Technical*

A Comparison Between Determinations of the Solubility of Oxygen in Oils by Exponential Dilution and Chemical Methods

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Abstract

The exponential dilution method has been tested as a rapid means for estimation of the solubility coefficient of oxygen in liquids. The relative standard deviation of the method was 5.7%. The method is not influenced by the presence of peroxides, which interfere with chemical oxygen determinations by ferrous-ferric ion titration. Values ranging from 0.07 to 0.17 were obtained for the coefficient of solubility of oxygen in raw and refined sunflower and soybean oils of different state of oxidation at room temperature.

Introduction

CHEMICAL METHODS for determination of the solubility of oxygen (1) have the advantage of being more rapid than physical methods (2,3), where the manometric measurements involved are time-consuming. Oxygen measurement with commercial amperometric instruments is a rapid procedure, but unfortunately tables currently available contain very little data on the solubility coefficients of oxygen in oils. As these coefficients are required for the calculation of oxygen content, exponential dilution was tested as a method for their determination.

Theory

The solute concentration C, after the addition of solvent of volume v, with adequate stirring, to a solution whose total volume V is kept constant, is related to the original concentration C_o by the following equation (4):

$$C = C_o \cdot e^{-v/V} \qquad [1]$$

If the vessel contains both a gas phase and a liquid phase, it can be shown that the concentration of a volatile solute in the gase phase is given by

$$C_g = C_{go} \cdot e^{-v/(V_g + kV_1)} \qquad [2]$$

when gas is passed through the vessel, provided that the distribution coefficient (k) of the solute is constant in the range of concentrations in question (5). V_g and V_1 represent the gas and liquid volumes. From equation (2), k can be calculated if the concentration in the gas phase is measured before and after a volume v of gas has been passed:

$$k = v/2.3(\log C_{g1} - \log C_{g2}) \cdot V_1 - V_g/V_1 \qquad [3]$$

It is also possible to calculate the total amount (W) of solute from two readings of the concentration:

$$W = \int_0^\infty C_g dv = C_{go}\,(V_g + kV_1) = C_{go} \cdot v_1/2.3 \cdot (\log C_{go} - \log C_{g1}) \qquad [4]$$

The general expression for W is

$$W = C_1 \cdot \frac{(v_2 - v_1)}{\ln(C_1/C_2)} \cdot (\frac{C_1}{C_2}) \exp\,(v_1/(v_2 - v_1)) \qquad [5]$$

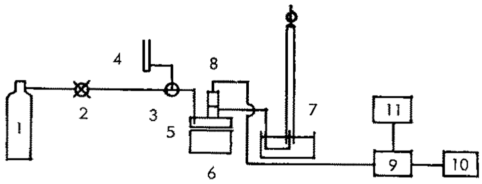

FIG. 1. Experimental set-up for determination of the distribution coefficient of oxygen by exponential dilution. 1) Inert-gas bottle with pressure reduction valve. 2) Gas flow regulator. 3) Three-way stopcock. 4) Soap-bubble flow meter. 5) Sample vessel. 6) Magnetic stirrer. 7) Gas buret. 8–10) Silvergold oxygen electrode with adapter and expanded-scale pH-meter (Beckman). 11) Recorder. The tubing between 3 and 5 should be short and narrow.

when the concentrations in the eluting phase C_1 and C_2 correspond to the volumes v_1 and v_2.

The relation between k and the Bunsen coefficient (α) is here given by

$$k = \alpha \cdot T/273 \qquad [6]$$

Experimental

Water was used as a reference solvent, for which the solubility of oxygen is thoroughly tabulated (6,7). The following oils were used a) refined sunflower seed oil, b) raw sunflower seed oil, c) refined soybean oil, d) the same, but oxidized by standing in daylight in contact with air at room temperature, e) raw soybean oil. Between determinations the samples were flushed with inert gas, and kept in full vessels in the dark at about 3C.

The experimental arrangement is depicted in Fig. 1, and in Fig. 2 the sample vessel used. The volume of the vessel up to the end of the electrode was measured, omitting the volume of the gas inlet tube. The vessel was filled to about 90% of its volume with liquid. Helium was used as the dilution gas, at a flow rate of 4–7 ml/min. The determinations were made at room temperature (22–23C). The gas volumes which had flowed through and the readings of the oxygen electrode were corrected for the pressure in the gas buret. Time required for determination is 5–10 min (Fig. 3).

Deviations from linearity of the log C vs. v plot were observed when large volumes of dilution gas were passed through. Better linearity was achieved with helium instead of heavier gases, like argon. The

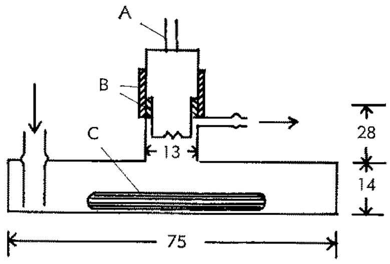

FIG. 2. Sample vessel. Materials: polymethacrylate, borosilicate glass, araldite. A) Cable. B) Rubber tubing. C) PTFE-covered iron rod. Dimensions are given in millimeters.

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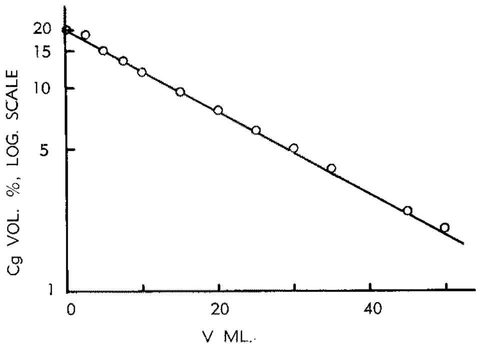

FIG. 3. Determination of O_2 solubility in raw sunflower oil by exponential dilution. Parameters: $V_1 = 68.9$ ml, $V_g = 8.77$ ml, t = 22C, dilution gas He, 5 ml/min k = 0.152.

shape of the vessels and the relative size of the residual gas volume in them also influenced the linearity. It was concluded that the deviations were caused by insufficiently rapid diffusion in the gas phase, rather than by nonlinearity of the distribution isotherm.

By differentiation of equation 3 with regard to V_g it is evident that, especially if k is small (<1), the relative error of k caused by errors in volume measurement becomes smaller when V_1 is increased with regard to the total volume of the vessel.

Chemical oxygen determinations were made by iodometric titration of ferric ion formed from a mixture of manganous and ferrous salts (1).

Peroxide-numbers were determined according to the AOCS Official Method Cd 8-53(8).

Results

By exponential dilution an average value of 0.031 was obtained for the distribution coefficient of oxygen between water and argon. The value calculated from literature values (7) is 0.0316. The estimated relative standard deviation (RSD) was 5.7%. The RSD estimated from the determinations on oil was 3%. The RSD for the chemical oxygen determinations was 7%.

The distribution coefficients obtained by exponential dilution, the oxygen contents calculated from these (when the oil was equilibrated with air), the results of the chemical oxygen determinations, and the peroxide values for oils oxidized to different degrees are presented in Table I. As is seen from the table, physical and chemical oxygen assays agree well if the peroxide value of the oil is low, whereas, with rising peroxide content in the oil, considerable differences are observed. The peroxide value of an oil sample which has been used for chemical oxygen assay is much lower than that obtained directly on the oil. Thus it seems evident that the chemical oxygen assay has measured not only the oxygen dissolved in oil, but also a large part of the hydroperoxides present. An attempt to correlate quantitatively the reagent consumption in the chemical oxygen assay with the sum of peroxide and dissolved oxygen content did not give accurate results, due possibly to differences in the course of oxidation of peroxides in the peroxide determination and the chemical oxygen assay, respectively.

TABLE I

Limits of Confidence at the 90% Level

Oil	Peroxide value mE/kg		Chemical O_2-determination	Exponential dilution method	
	Direct measurement on the oil	Measurement on oil previously subjected to chemical O_2-assay	$\frac{O_2\text{ml NTP}}{100\text{ ml}}$	k	$\frac{O_2\text{ml NTP}}{100\text{ ml}}$
A	0.3 ± 0.1	0.39 ± 0.1	1.8 ± 0.5	0.100	1.9 ± 0.3
B	61.3 ± 4	6.4 ± 0.1	14.7 ± 4.5	0.151	2.9 ± 0.1
C	61.3 ± 4	3.2 ± 0.6	14.1 ± 4 (should be 0)		
D	86.9 ± 5		22.7 ± 6		
E	<0.1		2.1 ± 0.7	0.070	1.3 ± 0.1
F	4.7 ± 0.6		2.0 ± 0.6		
G	8.1 ± 0.7	0.8 ± 0.1	3.3 ± 0.9		
H				0.173	3.2 ± 0.2

A, sunflower oil refined; *B*, sunflower oil raw; *C*, same as *B*, but dissolved O_2 removed with inert gas before determinations; *D*, Sunflower oil, raw, second sample; *E*, soybean oil refined; *F*, same as E, but oxidized; *G*, same as F, but further oxidized; *H*, soybean oil, raw.

It may be noted that the solubility of oxygen is higher in raw than in refined sunflower oil. A similar difference is observed with soybean oil. We do not yet know the cause of this.

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