The Solubility of Water in Edible Oils and Fats

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Abstract

The solubilities of water in rapeseed oil, coconut oil, and a palm-coconut oil mixture were determined at temperatures of 60C, 80C, and 100C.

Oil samples were equilibrated with water vapor under conditions of constant temperature and humidity. The equilibrium water content was determined by means of the Karl Fischer titration method.

The solubility was found to be independent of the type of oil when expressed in terms of the mole fraction. An equation relating solubility and temperature is given.

Introduction

Certain processes carried out in the edible oils and fats industry, such as hydrolysis and vacuum drying, are influenced by the amount of water dissolved in the oil or fat. Before tackling the problems of reaction and mass transfer connected with these processes it is desirable to have a knowledge of the solubility of water in triglycerides.

In the case of oil and water two separate although related types of equilibrium are important: a two-phase equilibrium between water in oil and water vapor, and a three-phase equilibrium between water in oil, liquid water, and water vapor. Both the two-phase and three-phase equilibria have previously been investigated (1–4), but no attempt has been made to correlate all these data.

Theory

Consider a non-ideal solution of water in oil in contact with a perfect gas phase containing water vapor. If the total pressure is low this assumption of a perfect vapor phase is quite reasonable. At equilibrium the activity of water is identical in both phases and thus:

$$P/P_s = \gamma x \qquad [1]$$

where the activity coefficient is defined by the convention $\gamma \rightarrow 1$ as $x \rightarrow 1$.

In this general relationship between the partial vapor pressure of water in the gas phase and the mole fraction of water in the liquid phase, P_s is dependent on temperature and pressure and γ is dependent on temperature, pressure, and composition. At low pressures the influence of the pressure on P_s and γ is negligible. For most solutions at low solute concentrations γ is also independent of composition, i.e., Henry's Law is obeyed. Under these conditions γ will vary only with temperature.

The excess Gibbs free energy of solution is defined as

$$\Delta G_e = \Sigma(n_i \, RT \ln \gamma_i)$$

and hence in this case:

$$\Delta G_e = -[n_f \, RT \ln \gamma_f + n \, RT \ln \gamma]$$

where $\gamma_f \rightarrow 1$ as $x_f \rightarrow 1$.

For solutions where the solute obeys Henry's Law, the solvent behaves ideally for all practical purposes. Hence we can consider $\gamma_f = 1$ and thus the excess Gibbs free energy of a solution of water in oil is given by:

$$\Delta G_e = -n \, RT \ln \gamma$$

or

$$\Delta g_e = -RT \ln \gamma \text{ per mole water dissolved.}$$

From the definition of the Gibbs free energy we know that

$$\Delta g_e = \Delta h_e - T\Delta s_e$$

and hence

$$\ln \gamma = -(\Delta h_e/RT) + (\Delta s_e/R) \qquad [2]$$

Over small ranges of temperature the excess heat and entropy of solution may be assumed to be constant.

If the water vapor pressure in the two-phase system is increased at constant temperature, more water will dissolve in the oil until the saturation water vapor pressure is reached. At this point water will start to condense and a three-phase system will be formed. The oil is then saturated with water at this temperature.

If Henry's Law is obeyed up to the saturation point, Eq. [1] also applies to the saturation solubility of water in oil. Substituting the saturation conditions $(P = P_s; x = x_s)$ in Eq. [1] we find

$$\gamma x_s = 1 \qquad [3]$$

This is equivalent to considering the activity of the water in the liquid water phase to be unity. This is not strictly true, since any oil which dissolves in the liquid water will affect the activity of this phase. However, the solubility of oil in water is very small (5) and for all practical purposes it is a valid assumption.

The effect of temperature on the saturation solubility of water in oil can be obtained by substituting [3] in [2]:

$$\ln x_s = (\Delta h_e/RT) - (\Delta s_e/R) \qquad [4]$$

Experimental Section

The solute isopiestic method was chosen to determine the solubility of water in edible oils under varying conditions of temperature and water vapor pressure. The principle of this method has been described by Christian et al. (6). The substance to be investigated is contacted via the gas phase with an aqueous solution or solid with a known water vapor pressure. Both sample and reference substance are maintained at the same temperature and equilibration takes place by transfer of water from the reference substance to the sample through the gas phase.

Apparatus

The apparatus used for most of the determinations consists of two 200-ml conical flasks connected by a normal laboratory distillation T-piece, one flask holding the oil sample and the other the reference solution—in our case aqueous solutions of sodium hydroxide (see Fig. 1). The whole apparatus was submerged up to the sampling joint in a constant temperature bath.

Samples were taken through the third arm of the

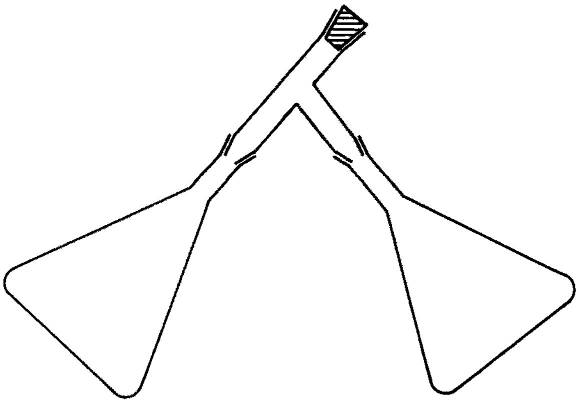

FIG. 1. Equilibrium apparatus.

T-piece using a 20-ml syringe with a steel needle. This helped to minimize the contact between oil and the atmosphere during the sampling and analysis procedure. It was necessary to keep the syringe at about the same temperature as the bath, to avoid condensation on the needle during sampling.

A disadvantage of this apparatus was the small interfacial area between the liquids and the gas phase which resulted in equilibration times of up to 80 hr. Care had to be taken to avoid "pseudo-equilibria"—apparent equilibria observed during an 8-hr working day.

When using NaOH solutions stronger than 80 g/100 g water, inconsistent results were obtained due to the reaction between the sodium hydroxide solution and glass (Jena G 20).

Procedure

A quantity of oil was placed in the apparatus and samples were taken at the same time for analysis of the initial water content, the acid value, and the saponification value. A NaOH solution of approximately the required concentration was made up, if necessary by warming. The solution was poured into the appropriate flask and, if warm, allowed to cool before attaching the flask with the oil sample. This procedure was followed to avoid condensation of water vapor on the cold glass and oil surfaces.

The two solutions were then allowed to equilibrate at constant temperature. For the first hour or two it was necessary to vent the system at regular intervals until the air was fully expanded and the water vapor pressure had built up. Samples were taken about every 3 hr and immediately analyzed for water by the Karl Fischer method. After consistent results had been obtained over a period of 24 hr, it was assumed that the system had come to equilibrium.

The final concentration of the NaOH solution was determined by titration. At the end of the first few experiments the acid value of the oil was determined again to check on the possibility of hydrolysis.

Analyses

The acid value and the saponification value were determined by a standard method (7). If it is assumed that fats and oils are for all practical purposes mixtures of triglycerides, their equivalent molecular weights can be calculated from their saponification values. This in turn enables values of % H_2O in oil to be converted into mole fractions.

The strengths of the NaOH solutions were determined by titrating a known weight of solution with HCl using phenolphthalein as indicator.

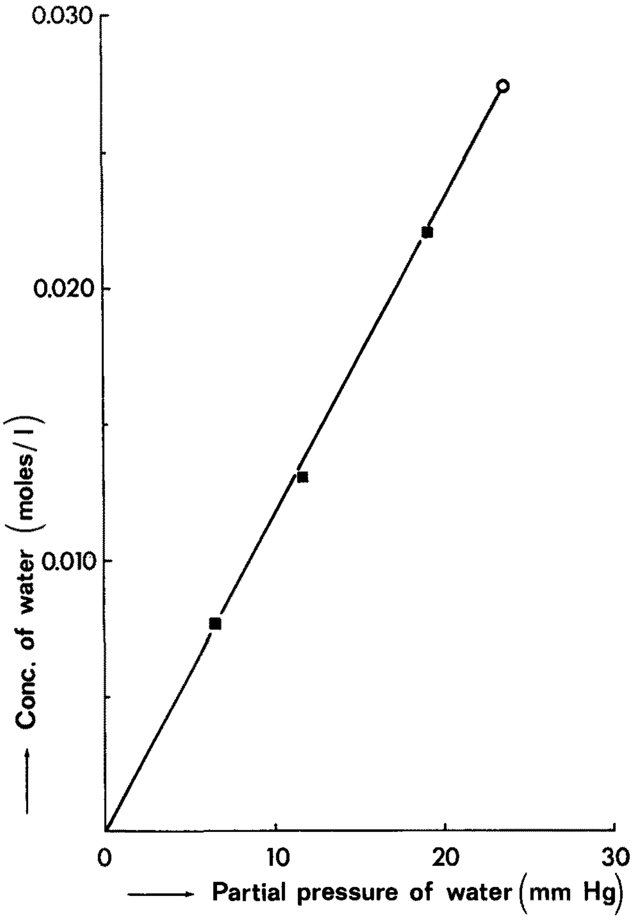

FIG. 2. Equilibrium between toluene and water vapor at 25C.—○ See Ref. 8. ■ This work.

The water contents of the oil samples were determined using the Karl Fischer dead-stop titration method. The syringe plus sample was accurately weighed after first flushing the syringe with the same oil. The required amount of solvent (methanol: chloroform, 2/3, v/v) was then buretted into the cell of a Metrohm E 408 and pretitrated with Karl Fischer reagent until the end-point reading remained steady for at least 10 sec.

The sample was added immediately after the pretitration and titrated following exactly the same procedure. These operations should be carried out as quickly as possible, to minimize absorption or desorption of water from sample or air. Finally the empty syringe was reweighed.

The water content of the sample can then be calculated using the following equation

$$\% \, H_2O = \frac{F.V.}{10.m} \, g \, H_2O/100 \, g \text{ sample}$$

The reagent was standardized by following the same procedure, a few drops of water from an eye dropper being substituted for the sample.

Since we knew we should be dealing with very low water contents, the apparatus and method were evaluated fairly critically before the experiments were even started. With low water contents the volume of reagent used controls the accuracy of the determination. Thus we looked for means of increasing the volume of reagent required and of

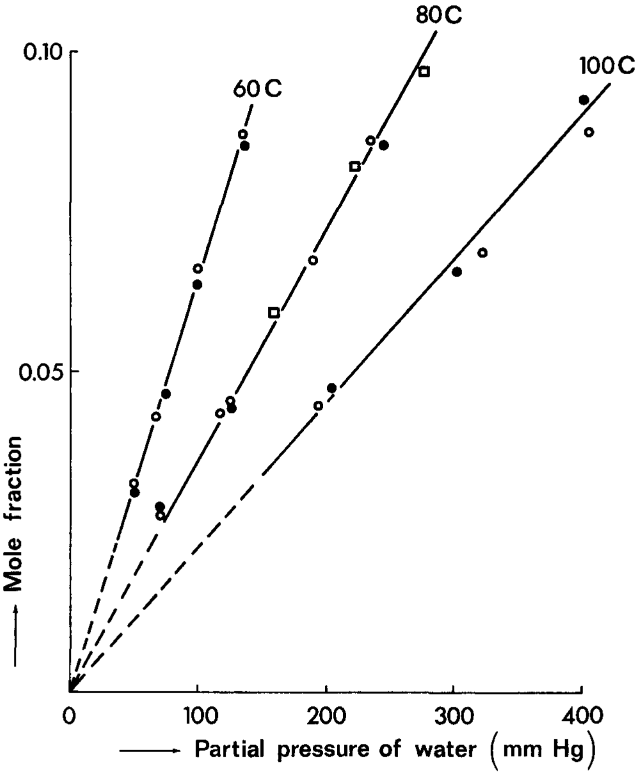

FIG. 3. Influence of temperature and partial vapor pressure of water on the mole fraction solubility of water in various oils. ○ Mixture of palm oil and coconut oil (60/40). ● Coconut oil. □ Rapeseed oil.

decreasing the minimum amount of reagent that could be titrated.

A finer capillary was fitted to increase the sensitivity of the burette.

By diluting the reagent the volume required for a given sample is increased. Reagents with F = 1 and F = 3 were tried, but it was found that with the Metrohm apparatus the sharpness of the end point was affected and there was no net improvement in accuracy compared with the normal F = 5 reagent. A larger sample also increases the volume of reagent required. Here we were limited to 10-g samples by the size of the cell and the amount of solvent required.

The accuracy of the reagent amounts used for the Karl Fischer method can be summarized as follows:

F about 5 mg water/ml reagent ±0.5%
m about 10 g ±0.05%
V ±0.02 ml

These figures suggest that the water content can be determined to within ±0.001% H_2O at low concentrations and this was in fact the variation observed.

Results

Water-toluene equilibrium

It was considered desirable to test the apparatus and method against published equilibrium data prior to investigating the oil-water equilibria. Determinations of the toluene-water vapor equilibrium at 25C (8) were repeated in our own apparatus and the results are given in Fig. 2. The agreement between the published and determined values is good. The partial pressures of water above the NaOH solutions were interpolated from data given by Robinson and Stokes (9).

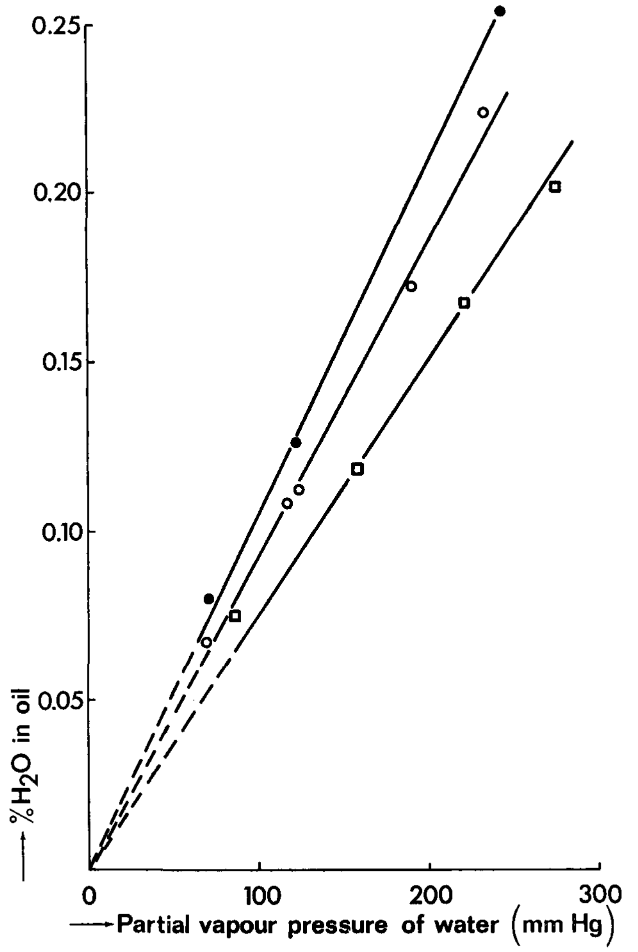

FIG. 4. Influence of oil type and partial vapor pressure of water on the weight percentage solubility of water in oils at 80C. ○ Mixture of palm oil and coconut oil (60/40). ● Coconut oil. □ Rapeseed oil.

Water-oil equilibrium

The equilibrium between water in oil and water vapor was investigated for coconut oil at 60C, 80C, and 100C, for rapeseed oil at 80C, and for a mixture of 60 wt/100 palm oil and 40 wt/100 coconut oil at 60C, 80C, and 100C. The oils used were fully refined.

The equilibrium values have been plotted in Fig. 3. The partial water vapor pressures were deduced from data tabulated in the Chemical Engineers' Handbook (Ref. 10).

For any specified temperature a plot of the partial vapor pressure of water against the mole fraction of water in any triglyceride oil gives rise to a single straight line. For comparison, the data at 80C have also been plotted as % H_2O against partial pressure in Fig. 4.

We may conclude that our assumption that the activity coefficient of water in oil is independent of composition was completely justified. Neither variations in the water content nor in the triglyceride composition of the oil have any significant influence.

Fatty acids can dissolve more water than their corresponding triglycerides (3). However, the oils used for the experiments had a very low fatty acid content and hydrolysis was negligible. It can be

TABLE I

Activity Coefficients of Water in Oil

Type of oil	Mol. wt (12)	Temp (C)	Sat. solubility % H_2O	x_s	Activity coeff.	Ref.
Cottonseed	876	32.2	0.138	0.0629	15.9	Parsons and Holmberg (2)
		22.5	0.121	0.0556	18.0	
		16.1	0.106	0.0490	20.4	
		10.0	0.090	0.0420	23.8	
		0	0.074	0.0347	28.8	
Tallow	852	100	0.27	0.1133	8.8	Lascaray (3)
Soybean	876	22	0.11	0.0508	19.7	Loncin (1)
		60	0.19	0.0847	11.8	
Coconut	654	60	0.285	0.0923	10.7	
Palm	846	60	0.23	0.0975	10.3	
Palm/coconut mixture	757 ± 2	60	....	....	10.3 ± 0.2	This work
		80	....	....	7.7 ± 0.3	
		100	....	....	6.0 ± 0.7	
Coconut	661 ± 1	60	....	....	10.7 ± 0.3	
		80	....	....	8.0 ± 0.6	
		100	....	....	5.7 ± 0.6	
Rapeseed	960	80	....	....	7.7 ± 0.8	

assumed that the fatty acids had no appreciable effect on the results.

For each oil/temperature combination the x-P data have beeen statistically fitted (11) to a straight line passing through the origin. The activity coefficients were then calculated from the slopes of these lines with the help of Eq. [1]. The values found are given in Table I.

Comparison with Published Data

Most of the reported investigations into the solubility of water in fats and oils have been devoted to the three-phase equilibrium. These published values of the saturation solubility were determined by various methods at temperatures between 0C and 100C. Loncin (1) centrifuged mixtures of water and oil at constant temperature until the water content of the oil phase was constant. Parsons and Holmberg (2) determined the critical solution temperature of samples of winterized cottonseed oil containing known amounts of dissolved water. The saturation solubility of water in tallow at 100C has been determined by Lascaray (3). A mixture of tallow and water at 100C was stirred and allowed to settle. A well-clarified sample of fat was then dried to constant weight.

Our own results at 60C and those of Okkerse (4) at 20C show that Henry's Law is obeyed up to the

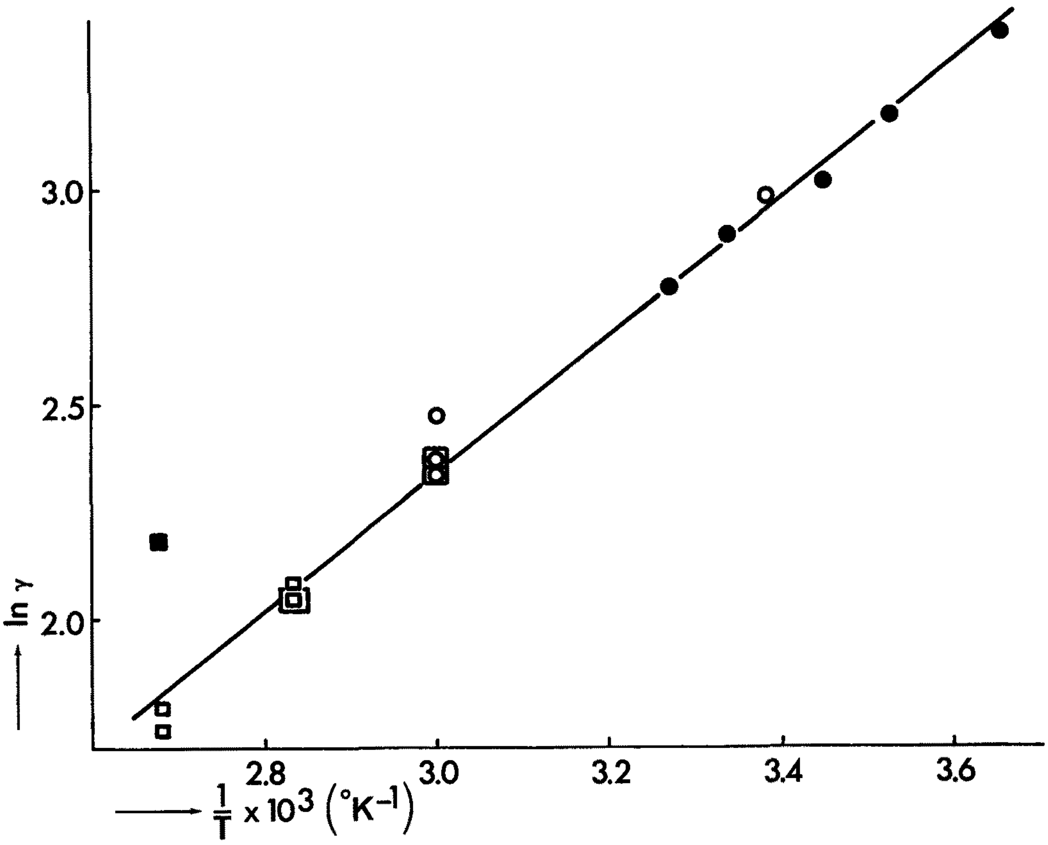

FIG. 5. Activity coefficient of water in oils as a function of temperature. ● Parsons and Holmberg (2) ■ Lascaray (3) ○ Loncin (1) □ This work.

saturation point. Hence Eq. [3] may be used to calculate the activity coefficients from the published results. Average molecular weights for the oils, deduced from saponification values given by Bailey (12), have been used to convert % H_2O into mole fractions. These results are also given in Table I.

All the data tabulated in Table I and graphically shown in Fig. 5, with the exception of the single result of Lascaray, have been statistically fitted (11) to a line of the form given by Eq. [2]. This resulted in the following equation:

$$\ln \gamma = \frac{1{,}600 \pm 40}{T} - 2.5 \pm 0.5$$

from which the excess entropy and excess enthalpy of solution may be calculated.

$$\Delta h_e = -3{,}180 \pm 80 \text{ cal/mole}$$
$$\Delta s_e = -4.9 \pm 1.0 \text{ cal/mole °K}$$

Okkerse (4) investigated the equilibrium between water vapor and water in groundnut oil between 20C and 50C. From his results it can be deduced that

$$\Delta h_e = -3{,}200 \text{ cal/mole}$$
$$\Delta s_e = -4.0 \text{ cal/mole °K}$$

which are in good agreement with our own values.

Discussion

Within the bounds of experimental error the solubility of water in liquid oils and fats is independent of the type of oil or fat considered, when expressed in terms of the mole fraction. For the three-phase equilibrium between water vapor, liquid water, and water in oil, the solubility is given by

$$\ln x_s = 2.5 - \frac{1{,}600}{T} \qquad [5]$$
$$273°K < T < 373°K$$

For the two-phase equilibrium between water vapor and water in oil the solubility is given by

$$\ln \frac{xP_s}{P} = 2.5 - \frac{1{,}600}{T} \qquad [6]$$
$$273°K < T < 373°K$$

At present the correlation can be claimed to apply only to (mixtures of) triglycerides with average molecular weights between 650 and 960. It is well known that the chain length influences the physical properties of low molecular weight compounds in a homologous series and this will no doubt be true for the solubility of water in low molecular weight triglycerides. However, it seems reasonable to assume that Eq. [5] and [6] will also hold for the separate components of the mixtures investigated.

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List of Symbols

Unless otherwise stated the relevant symbols in the text refer to water.

R	Gas constant	1.987 cal/mole °K
T	Absolute temperature	°K
γ	Activity coefficient	
x	Mole fraction	
P	Partial vapor pressure	mm Hg
G	Gibbs free energy	cal
n	Number of moles	
g	Molar Gibbs free energy	cal/mole
h	Molar enthalpy	cal/mole
s	Molar entropy	cal/mole °K
M	Molecular weight	
% H_2O	g Water per 100 g wet oil	
F	Karl Fischer reagent factor	(mg water per ml reagent)
V	Volume Karl Fischer reagent	ml
m	Weight of oil sample	g

Subscripts

s	Saturation state
i	Component i
f	Oil or fat
e	Excess thermodynamic function of mixing

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