

The Solubility of Water in Edible Oils and Fats Above 100 C

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ABSTRACT

The solubilities of water in rapeseed and coconut oils have been determined at temperatures between 90 and 160 C. 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. Solubility was found to be independent of the type of oil when expressed in terms of the mole fraction, in agreement with previous work at temperatures below 100 C. An equation is given relating solubility and temperature between 0-250 C.

INTRODUCTION

A knowledge of the solubility of water in edible oils and fats above 100 C is necessary for the analysis of processes such as oil drying and fat splitting.

Previous work in this laboratory (1) which verified the thermodynamic basis of water in oil solutions was limited to temperatures below 100 C due to the method employed. The recent development of a more flexible method has allowed the study of solubilities to be extended up to temperatures of 160 C.

EXPERIMENTAL PROCEDURES

The isopiestic method used previously (1) suffered from long equilibration times (up to 80 hr) and the corrosive nature of the reference solution (aqueous NaOH). The method employed in the present work is similar to the transpiration method for the determination of vapor pressures. The same method was used by Okkerse (2) for the determination of the heat and entropy of solution of water in peanut oil.

In principle, a carrier gas saturated with a vapor is bubbled through the liquid to be investigated. Vapor is transferred from the gas phase to the liquid until equilibrium is reached. The temperature of the liquid must be higher than the saturation temperature of the vapor.

Equilibration can be achieved within 1-2 hr which is a

great improvement over the isopiestic method. However, the greatest care must be taken in designing and operating the apparatus.

Apparatus

For our purpose nitrogen was bubbled through three 1-liter round-bottomed flasks connected in series and immersed in separate thermostat baths (Fig. 1). The first two flasks contained water. The temperature of the first flask (presaturator) was maintained about 5 C above that of the second flask (saturator) to ensure that the resulting stream of gas was fully saturated with water vapor at the saturator temperature. The third flask (equilibrator) contained oil at a temperature above that of the saturator.

The gas lines between the flasks were electrically heated to prevent condensation and the gas was distributed in the liquids through sintered glass discs.

Each flask had three necks, two of which were used for the gas inlet and outlet; the third was available for temperature measurement. The equilibrator had a fourth neck to enable samples of the oil to be taken without disturbing the flow system.

Temperatures were measured with mercury in glass thermometers, in the equilibrator to within 0.1 C and in the saturator to within 0.2 C.

The nitrogen was supplied from a cylinder under pressure through a reducing valve. The actual flow was measured and adjusted by means of a rotameter and needle valve. Before entering the presaturator the nitrogen was passed through a buffer flask to smooth out any pressure or flowrate fluctuations.

Procedure

The appropriate flasks were half-filled with oil or water and the equilibrator thermostat was set at the required temperature. When the oil had reached about 50 C the gas flow was started and adjusted to a steady rate of about 17 liters/hr. The required water vapor pressure was then chosen and the saturator thermostat set at the corresponding saturation temperature. The presaturator thermostat was adjusted to approximately 5 C higher.

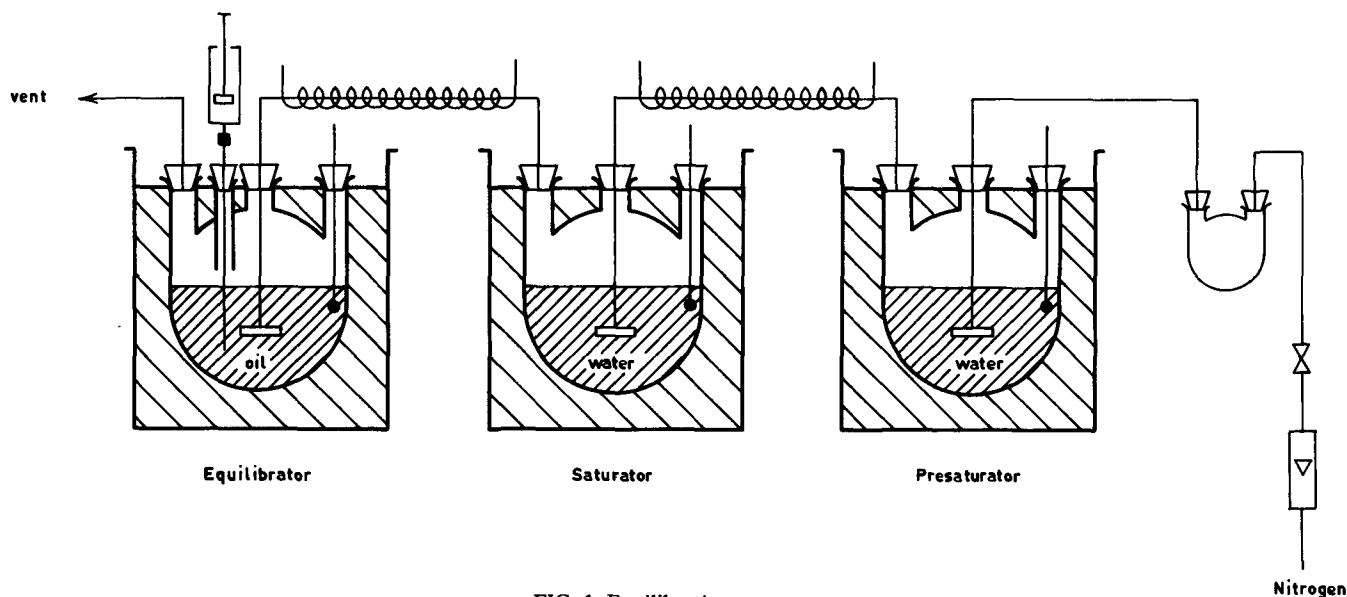


FIG. 1. Equilibration apparatus.

TABLE I
Activity Coefficients of Water in Oil

Type of oil	Molecular weight	Temperature, C	Saturation solubility		Activity coefficient γ
			% H ₂ O	x_s	
Coconut	665 ± 2	92	---	---	6.46 ± 0.16
		120	---	---	4.53 ± 0.20
		140	---	---	3.36 ± 0.09
		161	---	---	2.55 ± 0.12
Rapeseed	962 ± 3	121	---	---	4.65 ± 0.11
		140	---	---	3.40 ± 0.11
		161	---	---	2.51 ± 0.13
Peanut (4)	884	244	4.3	0.688	1.45
		250	4.8	0.712	1.40
		262	5.2	0.729	1.37
		265	6.7	0.779	1.28

Samples of oil (ca. 10 ml) were taken at regular intervals and immediately analyzed for their water content by the Karl Fischer method. The samples were taken using a syringe which could be connected to a capillary needle permanently mounted in a rubber bung in the fourth neck of the equilibrator. The same precautions were observed as in the previous study (1). After three consistent results had been obtained the system was assumed to have reached equilibrium. The oil and saturator temperatures were noted before each sampling.

Samples were also taken for determination of the acid value and saponification value of the oil.

RESULTS AND DISCUSSION

To obtain valid results using the transpiration method the gas entering the equilibrator must be fully saturated with water vapor at the saturator temperature. This requirement was checked by studying the efficiency of saturation under various conditions of temperature and flowrate. The equilibrator was disconnected and replaced by two silica gel tubes mounted in series. By measuring the gain in weight of the silica gel tubes and the nitrogen flow over a known time interval the water vapor pressure could be calculated and compared with the saturation value.

The ratio of measured and saturation vapor pressures was determined at a gas flowrate of about 20 liters/hr and at temperatures between 40-80 C. The mean and standard deviation of five determinations was 0.962 ± 0.039 . Another series of experiments in the same temperature range but at flowrates of between 5-25 liters/hr gave no indication that the saturation efficiency was dependent upon gas flowrate. However, at higher flowrates, inconsistent results were obtained due to the formation of a mist in the gas stream.

It was concluded that, within the experimental error, the gas stream leaving the saturator was fully saturated with water vapor at the saturator temperature.

Water-Oil Equilibrium

The equilibrium between water in oil and water vapor was investigated for coconut oil and rapeseed oil at about 90, 120, 140 and 160 C. The oils used were in all cases fully refined.

The results of these experiments are shown in Figure 2. No significant hydrolysis was observed which could have influenced the results (acid value, 0.17-0.27).

As was observed in the previous study (1), for any specified temperature, a plot of the partial vapor pressure of water against the equilibrium mole fraction of water in any oil gives rise to a single straight line. Within the experimental range of vapor pressure (60-520 mm Hg) and temperature (90-160 C) the mole fraction solubility of

water in oil is therefore independent of composition.

The general equilibrium relationship between the vapor pressure (P) in the gas phase and the mole fraction solubility (x) in the liquid phase is (1)

$$\frac{P}{P_s} = \gamma x$$

where P_s is the saturation vapor pressure of water and γ the activity coefficient of water in oil at the equilibrium temperature.

The activity coefficients for each oil temperature combination in Figure 2 were calculated using the above expression and are presented in Table I. Values of the saturation vapor pressure of water used throughout this study were taken from the "Handbook of Chemistry and Physics" (3).

It has already been mentioned that the equilibration

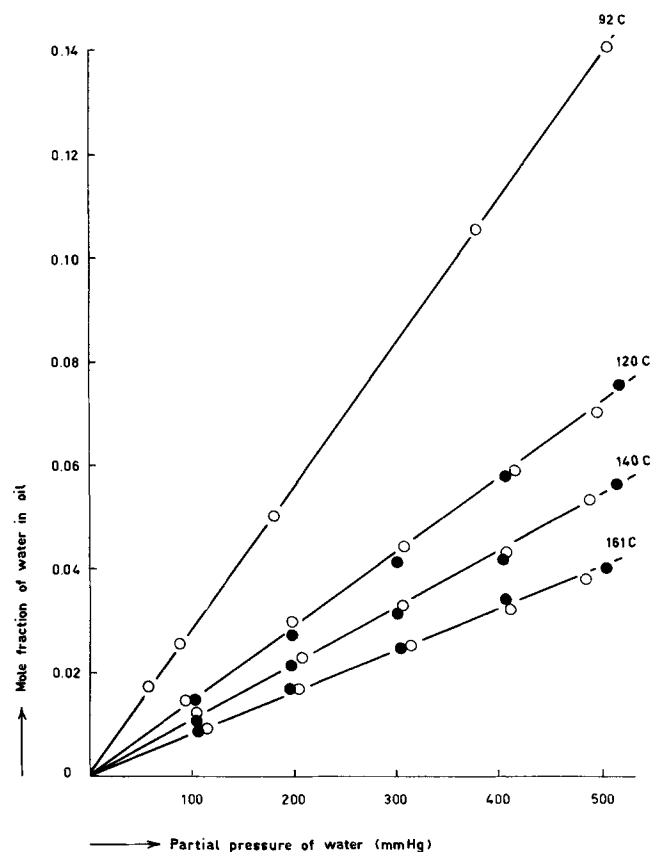


FIG. 2. Solubility of water vapour in oils. ○ Coconut oil, ● Rapeseed oil.

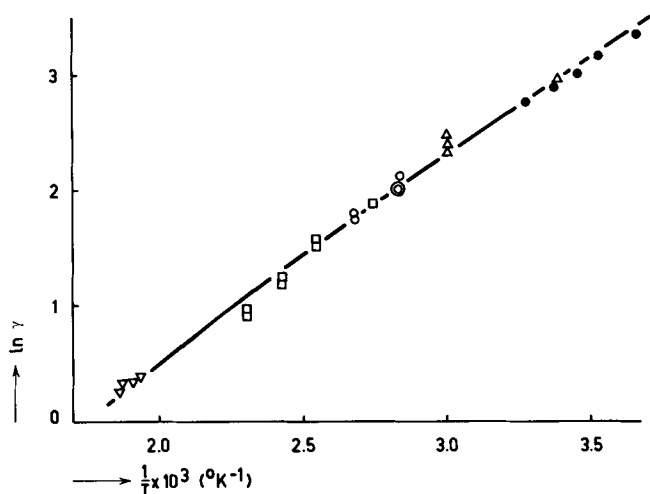


FIG. 3. Activity coefficient of water in oil as a function of temperature, ●, Parsons and Holmberg (5); △, Loncin (6); ○, Hülder (1); □, Present work; ▽, Van der Sluijs (4).

time using the transpiration method was about 2 hr compared with up to 80 hr for the isopiestic method. In addition the transpiration method ($\gamma \pm 0.15$) was found to be more accurate than the isopiestic method ($\gamma \pm 0.5$) (1).

Correlation of the Data

In Figure 3 all the known data on the solubility of water in oil are plotted as a function of temperature.

Van de Sluijs (4) has measured the saturation solubility of water in peanut oil containing 1-2% free fatty acid at about 250 C. The experiments were carried out in a wetted wall column in which a thin film of oil was contacted with liquid water. The contact time of the oil film with the water was about 60 s which was calculated to be sufficient for equilibration. The data of Van de Sluijs are included in Table I and Figure 3. The corresponding activity coefficients were calculated using the previously derived (1) saturation point relation

$$\gamma x_s = 1$$

The plot of $\ln \gamma$ against T^{-1} over such a large temperature range (0-250 C) can no longer be accurately represented by a straight line. The data have therefore been fitted to give the following three-term equation.

$$\ln \gamma = \ln \left[\frac{P}{x \cdot P_s} \right] = 7.118 + \frac{1222}{T} - 1.459 \ln T$$

The standard error of estimation of $\ln \gamma$ is ± 0.068 and the equation is shown as a full line in Figure 3.

The above correlation is based on the assumption that the author's gas-liquid equilibrium data can be combined with the liquid-liquid equilibrium data of previous investigators (4-6), i.e., activity coefficients are assumed to be

independent of composition up to the saturation point. This assumption has been proved to be valid at low temperatures (1) but it is possible that deviations occur at higher temperatures. This tendency is already apparent in Figure 3 and the reliability of the correlation is expected to decrease above 150 C.

Solubility Above 160 C

The solubility of water in oil at higher temperatures and pressures, such as are experienced in fat splitting columns, is difficult to measure since at temperatures around 200 C the rate of hydrolysis is appreciable. Van de Sluijs (4) has developed a feasible method but gave no indication of the accuracy of his data.

It must be expected that for gas-liquid equilibrium at high temperatures and pressures, nonideality of the gas phase and a concentration dependence of the activity coefficient will have to be taken into consideration.

Until now measurements have shown a linear relation between mole fraction and vapor pressure. If the oil water system exhibits a consolute point (critical solution temperature), then

$$\left(\frac{dP}{dx} \right)_T = 0 \text{ and } \left(\frac{d^2P}{dx^2} \right)_T = 0$$

and therefore the P-x curve will lose its linear character at some stage.

It is suspected that the activity coefficient obtained from gas-liquid equilibrium measurements will deviate at high temperatures from those obtained from liquid-liquid equilibrium measurements. Such a deviation would be a direct result of concentration dependence, since the gas-liquid studies are carried out under conditions of "infinite dilution" whereas the liquid-liquid equilibrium measurements refer to saturation conditions. Some systems are known which do not exhibit a consolute point (e.g., $\text{CHCl}_3\text{-H}_2\text{O}$) because the critical point of one of the components is reached first. Even if this applies to the water-oil system the possibility of concentration dependence at high temperatures cannot be excluded.

ACKNOWLEDGMENT

J.R. Bowgen did experimental work.

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