Diffusivities of Hydrogen and Glyceryl Trioleate in Cottonseed Oil at Elevated Temperature

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ABSTRACT

The diffusivities of hydrogen and glyceryl trioleate in cottonseed oil were determined at different iodine values. The diffusivity of hydrogen was shown to be ca. 100 times as great as that of the glyceryl trioleate. The diffusivities were shown to be dependent upon the iodine values. This influence could be explained, at least in the case of the glyceryl trioleate diffusion, by the difference of the viscosity of the oil. A separate determination of the solubility of hydrogen in the oil was a necessary part of the diffusivity determination.

INTRODUCTION

The mass transfers of hydrogen molecules and triglycerides molecules to the surface of the catalyst are important steps in the fat hydrogenation process. To calculate the driving force of these steps, a general relationship, including the physical properties and the flow variables, is needed. This relationship is difficult to formulate if important physical properties are unknown. One of the most important properties in this respect is the diffusivity. Little is known about the diffusivities of hydrogen and triglycerides in vegetable oils; and, in fact, this property is rather difficult to estimate with sufficient accuracy from general transport equations in the literature. In this article, the diffusivities of hydrogen and glyceryl trioleate in cottonseed oil were determined under conditions corresponding to the industrial fat hydrogenation process. Since the determination of the hydrogen diffusivity presupposes that the solubility of hydrogen in oil is known, a separate determination of this solubility also was carried out.

DIFFUSIVITY OF HYDROGEN IN COTTONSEED OIL

Experimental Procedures

The determinations were carried out using a modification of the diaphragm cell method developed by Tham, et al., (1) intended for the rapid determination of the diffusivity of a sparingly soluble gas in a liquid. The cell is divided into two compartments by a glass diaphragm. Hydrogen flows continuously through the oil in one of the compartments of the cell to keep the oil saturated with hydrogen. Nitrogen flows through the other compartment to expel quantitatively the hydrogen transported through the diaphragm from the first compartment. The concentration of hydrogen in the second compartment is negligible compared to that in the first compartment. The hydrogen concentration of the outlet gas from the cell was determined using a gas chromatograph. From this determination and the gas flow rate of nitrogen, it is possible to calculate the rate of hydrogen transported inside the diaphragm. The transport was considered to be an ordinary diffusion. Other transport mechanisms were not taken into consideration. The diaphragm was assumed to be equal to parallel cylinders, (2) all of the same size and filled with stagnant oil. If the mean length of the pores is L and the total pore area perpendicular to the length is A, the transport rate N at steady state can be written:

$$N = A\ D_H(c/L) \qquad [1]$$

where c is the hydrogen concentration in the first compartment from which hydrogen is transported and D_H is the diffusivity of hydrogen in the oil. The glass diaphragm was 2 mm thick with a pore width of 5 μ. The diaphragm cell was calibrated in an ordinary way (3) using 0.1 M aqueous potassium chloride. This calibration gives the quasistationary cell constant β defined by:

$$\beta = (A/L)[1/V_1) + (1/V_2)] \qquad [2]$$

where V_1 and V_2 are the volume of the cell compartments. Different cells were used in the present determinations. The volume of the cell compartments was of the magnitude of 400 cm^3.

Material

The cottonseed oil was bleached with Fuller's earth and heated under vacuum to remove water. The hydrogenated

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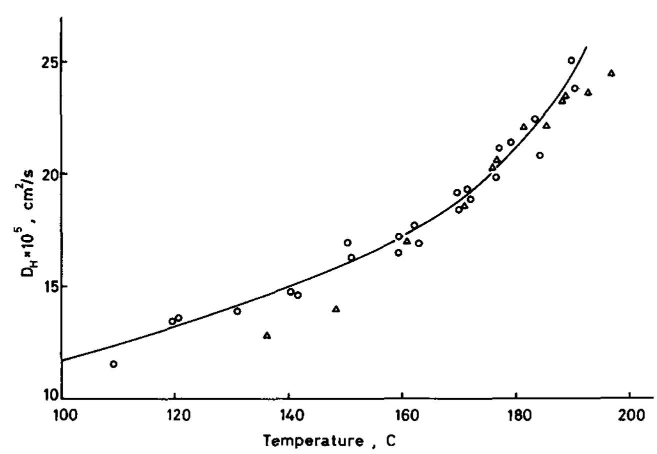

FIG. 1. The diffusivity of hydrogen in cottonseed oil. o = Cottonseed oil, iodine value 108, and Δ = hydrogenated cottonseed oil, iodine value 22.

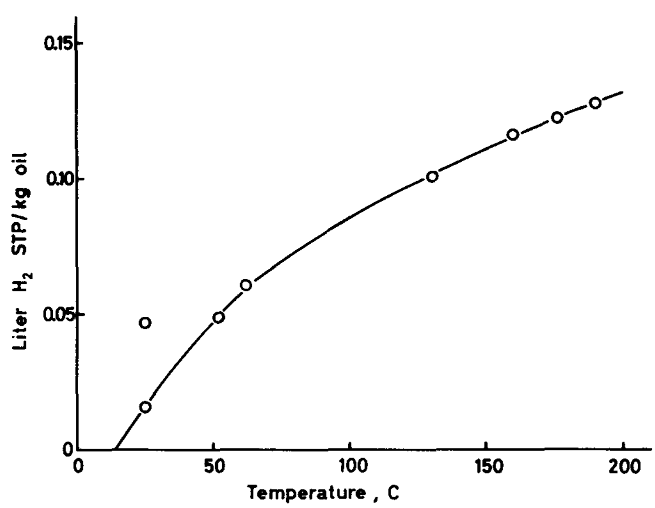

FIG. 2. The solubility of hydrogen in cottonseed oil at 1 atm hydrogen pressure.

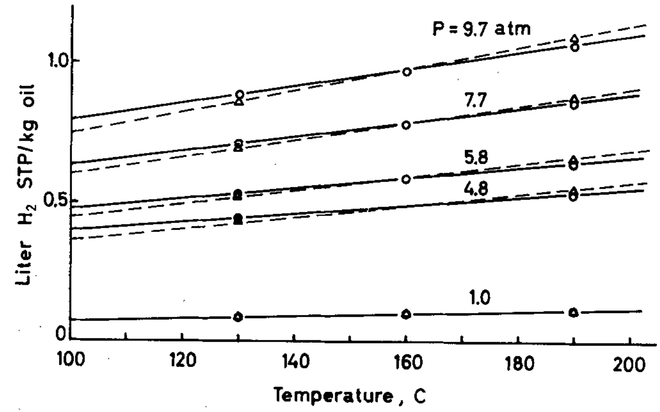

FIG. 3. The solubility of hydrogen in cottonseed oil. o = Cottonseed oil, iodine value 109, and Δ = hydrogenated cottonseed oil, iodine value 37.

cottonseed oil was obtained after conventional hydrogenation at 160 C using nickel as a catalyst.

Results and Discussion

Only a few determinations of the diffusivity of hydrogen in liquid phase at elevated temperature have been published hitherto (4); therefore, the method of diffusivity determination used here could not be checked at the temperature interval of interest. The method was, instead, checked by determining the diffusivity of hydrogen in water at 25 C. The determination was carried out with two different cells; and the mean diffusivity obtained was $(5.0 \pm 0.03) \times 10^{-5}$ cm^2/s, which is in good agreement with literature date (5-13).

The diffusivity determinations were carried out with cottonseed oil (IV=108) and hydrogenated cottonseed oil (IV=22) at 100-200 C. The result is given in Figure 1. It is obvious from the result that the diffusivity depends upon the iodine value of the oil. This dependence cannot be explained by the difference in viscosity between oils at different iodine value, since it was found that the diffusivity of hydrogen was not proportional to T/μ, where T is the absolute temperature and μ is the dynamic viscosity. This proportionality is valid in the well known Stokes-Einstein equation (14) and in the equation by Wilke and Chang (15). Using Wilke and Chang's equation, the calculated diffusivity at 180 C will be $D_H = 8.6 \times 10^{-5}$ cm^2/s, which may be compared with the found value $D_H = 22 \times 10^{-5}$ cm^2/s. This deviation between calculated and found values generally is obtained for the diffusivity of hydrogen in different liquids (16, 17). The difference is often much higher than that found in the present experiments.

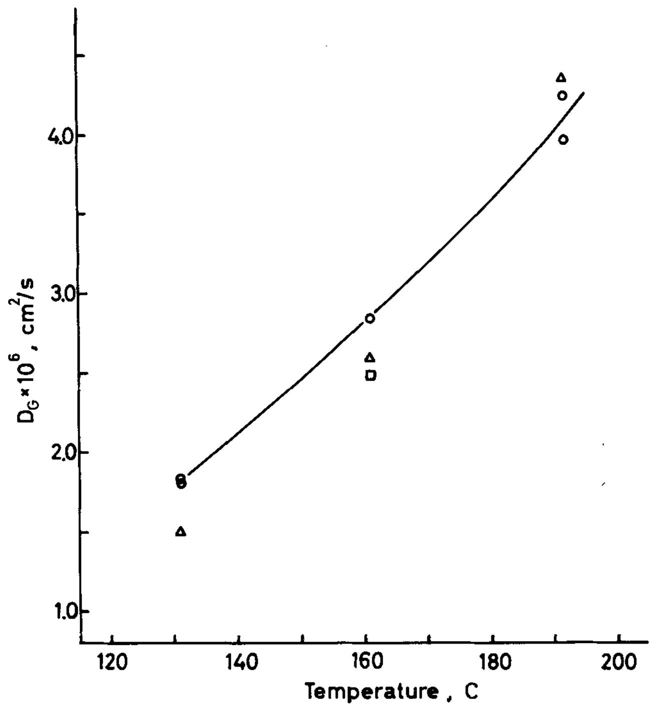

FIG. 4. The diffusivity of glyceryl trioleate in cottonseed oil. o = Cottonseed oil, iodine value 109, □ = hydrogenated cottonseed oil, iodine value 90, and Δ = hydrogenated cottonseed oil, iodine value 68.

SOLUBILITY OF HYDROGEN IN COTTONSEED OIL

The determination of the diffusivity of hydrogen in the oil presupposed that the solubility of hydrogen is known (see equation 1). The hydrogen concentration in the first compartment of the diaphragm cell is difficult to determine carefully, so the solubility should be determined separately. The solubility of hydrogen in vegetable oils was determined by Parson (18) at different temperatures and at a hydrogen pressure of 1 atm. Similar determinations were reported by Tyutyunnikov and Novitskaya (19, 20). Wisniak and Albright (21) determined the solubility at elevated pressure (10-100 atm) and at temperatures below 140 C. In the present study, the solubility of hydrogen in cottonseed oil and hydrogenated cottonseed oil was determined at 25-200 C and at hydrogen pressures of 1-10 atm.

Experimental Procedures

The solubility determinations were carried out in a steel autoclave of 1.6 l capacity, provided with an effective stirrer. After ca. 30 min of intense stirring, the oil was shown to be saturated with hydrogen, and an oil sample was withdrawn to an evacuated glass flask. The hydrogen was found to expel completely on sampling. The flask then was filled with nitrogen. The flask was cooled and weighed, and the temperature and pressure of the gas were determined carefully. A sample of the gas was analyzed with respect to the hydrogen content using a gas chromatograph.

Results and Discussion

The results of these determinations are given in Figures 2 and 3. Similar to other solubility data of hydrogen in vegetable oils given in literature, the solubility is given in the units liter H_2 STP/kg oil. In Figure 2, the solubility in cottonseed oil (IV=109) is given at different temperatures and at a hydrogen pressure of 1 atm. At temperatures of interest from an industrial point of view, the solubility may be approximated as a linear function of temperature. This function may be written:

$$c = (47.04 + 0.294\ t) \times 10^{-3}\ p \qquad [3]$$

where

t is the temperature in C, within the interval 130-190 C; p is the hydrogen pressure in atm (within the interval 1 and 10 atm); and c is the hydrogen concentration in 1 STP/kg oil.

The maximum deviation between calculated and found solubilities amounts to 0.5%. In Figure 3, the solubilities of hydrogen in cottonseed oil and hydrogenated cottonseed oil (IV=37) are given at different pressures and temperatures. The solubility is nearly independent of the iodine value of the oil. If consideration is taken of the solubility in hydrogenated oil, equation 3 will be:

$$c = (40.06 + 0.337\ t) \times 10^{-3}\ p \qquad [4]$$

The maximum deviation between calculated and found solubility amounts to 1%. It is not easy to compare the solubilities of hydrogen given in literature with those given in the present investigation, since the experimental conditions are quite different.

DIFFUSIVITY OF GLYCERYL TRIOLEATE IN COTTONSEED OIL

The diffusivity was determined using the diaphragm cell method in its original performance (2). The two compartments of the cell contain the same cottonseed oil except for a tracer amount of radioactive triglyceride in the first compartment.

Experimental Procedures

Diaphragm cell: The volume of the two compartments was 130 cm^3 each. The glass diaphragm was 2 mm thick with a pore width of 5 μ. Both compartments have plane bottoms with magnetic stirrers rotating 60 rpm.

Analytical methods: The radioactivity of the oil was determined using a liquid scintillation counter (Packard 3310). A weighed amount of oil (not more than 250 mg) was dissolved in 10 ml toluene, and 10 ml scintillation solution was added. The scintillation solution consists of 3 g 1,4-bis-2(4-methyl-5-phenyloxazolyl)-benzene and 0.5 g 2,5-diphenyloxazol dissolved in 1 liter of toluene. The rate of counted scintillations was found to be proportional to the amount of radioactive triglyceride up to 250 mg oil dissolved. A higher content of oil in the toluene solution quenches the scintillations.

Radioactive triglyceride: Glyceryl-tri-(oleate-1-C14) delivered from Radiochemical Center, Amersham, England, was used as a radioactive tracer. The triglyceride (0.1 m Ci) was dissolved in toluene.

Material: The same oil was used as in the other experiments reported in the present paper.

Results and Discussion

The determination was carried out in a conventional manner. The time needed to reach steady state conditions was ca. 24 hr. The diffusivity was calculated from the equation:

$$\ln(\Delta c_f/\Delta c_o) = \beta\, D_G \theta \qquad [5]$$

where Δc_f is the difference in radioactivity between the oil in the two compartments of the cell at the end of the experiment and Δc_o is the corresponding difference at the start of the experiment. β is the quasistationary cell constant defined by equation 2, and θ is the time. D_G is the diffusivity of glyceryl trioleate.

The determination of the diffusivity was carried out with cottonseed oil at different iodine values and in the temperature interval 132-192 C. Figure 4 shows that the diffusivity is dependent upon the iodine value of the oil. The influence of the iodine value probably is explained by the fact that the viscosity of the oil is dependent upon the iodine value. As may be seen from Figure 5, the diffusivity is proportional to T/μ, which is in accordance with the well known Stokes-Einstein equation (14). Since the relationship between the viscosity, temperature, and iodine value is known from determinations by Wakeham and Magne (22) among others, it is obvious that the diffusivity of the triglycerides may be calculated from Figure 5 if only the temperature and the iodine value are known.

A comparison of the diffusivities of hydrogen and triglycerides in cottonseed oil shows that hydrogen molecules diffuse ca. 100 times as fast as triglyceride molecules do.

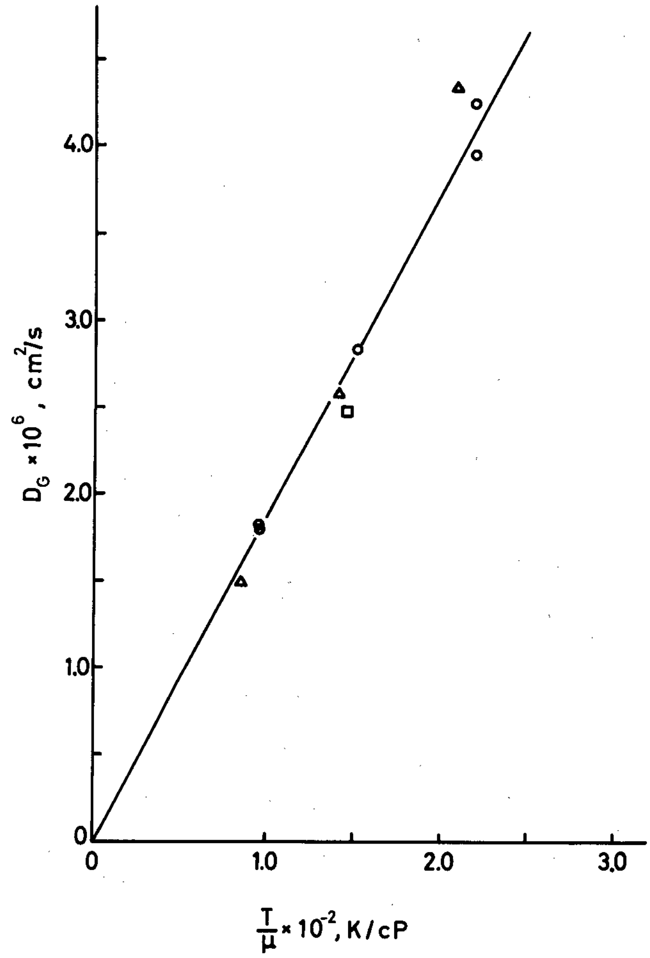

FIG. 5. D_G as a function of T/μ. o = Cottonseed oil, iodine value 109, □ = hydrogenated oil, iodine value 90, and Δ = hydrogenated oil, iodine value 68.

ACKNOWLEDGMENT

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