Measurement of the Diffusion Coefficient of Free Fatty Acid in Groundnut Oil by the Capillary-Cell Method

G. SMITS, Unilever Research, Vlaardingen, The Netherlands

ABSTRACT

A capillary-cell method has been used for measuring the diffusion coefficients of oleic and stearic acids in groundnut oil at 130 C. The method demands careful fulfillment of the boundary conditions and, therefore, special attention has been paid to the establishment of the appropriate experimental conditions. Despite the suggestions of previous workers, a lot of effort is required to approximate the ideal conditions adequately. The experimental conditions proved to be optimal when capillaries with an inner diameter of 0.8 mm and a length of 20 mm were placed in a stationary solvent bath. The diffusion coefficients of oleic and stearic acid are $(4.2 \pm 0.16)10^{-10}$ and $(3.7 \pm 0.23)10^{-10}$ m²/s, respectively, at a confidence interval of 95%.

INTRODUCTION

In the refining of edible oils, the alkali neutralization—removal of free fatty acids (FFAs) from oil by contacting it with (dilute) lye—is an important process step. The extraction efficiency and the percentage of neutral oil losses depend on the process conditions, type, and quality of the oil and on the amount of FFAs to be removed. To get a more quantitative insight into the various factors determining this process, the mass transfer mechanism should be analyzed.

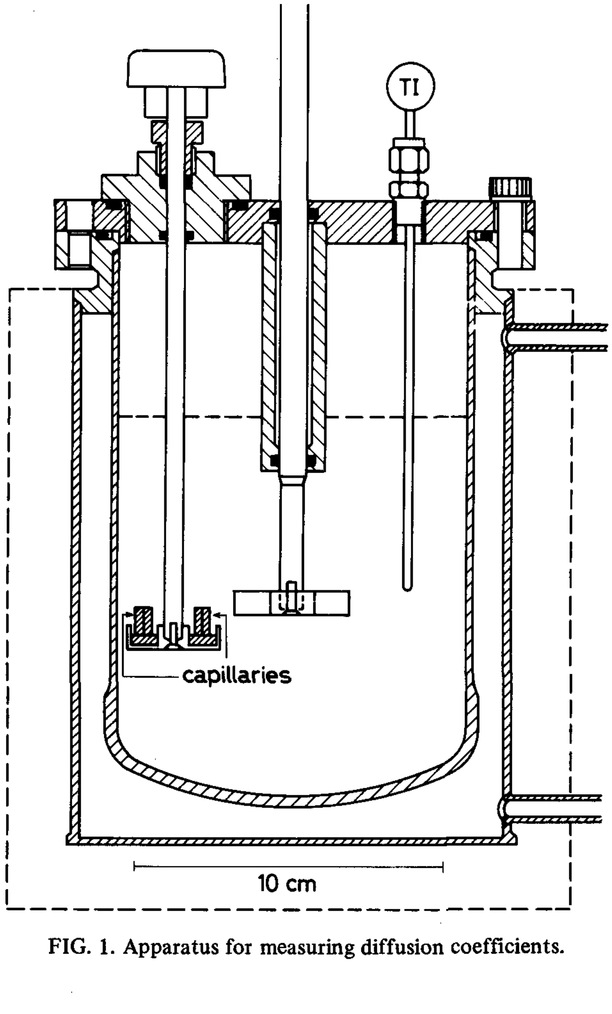

FIG. 1. Apparatus for measuring diffusion coefficients.

The transport of FFAs in the oil phase is generally considered as the rate-determining step. Thus, for a quantitative description, a fairly exact value of the diffusion coefficient is needed to be able to discriminate between the various mass transfer models and to establish to what extent the transport in the oil phase is really rate-determining under different process conditions.

Until now, no experimental measurements of the diffusion coefficient of FFAs in oil have been reported. Besides, this parameter is rather difficult to estimate with sufficient accuracy from general correlations from the literature. We measured the diffusion coefficient of oleic and stearic acid in groundnut oil at the rather high temperature of 130 C which is used in one of the common neutralization processes (1).

EXPERIMENTAL PROCEDURES

Method

For the measurement of the diffusion coefficient in liquid systems, several experimental methods are available (2), of which the diaphragm-cell method is recently most applied. However, we rejected this method because a calibration is needed to determine the cell constant. This calibration is generally performed with an aqueous solution and introduces a serious error by application to our system which involves a lower diffusion coefficient as well as a higher viscosity. Therefore, we used the capillary-cell method because this method is based upon the application of Fick's second law of diffusion to a well-defined geometrical system which abolishes calibration. In this method, designed by Anderson and Saddington (3) and further developed by Wang (4), a capillary closed at one end and filled with a solution containing the solute under study is placed in a large bath of the pure solvent. The diffusion coefficient may be calculated from (4):

$$D = 4l^2/(\pi^2 t) \ln [8/\pi^2 (C_o/C_t)] \qquad \text{(I)}$$

where l = length of the capillary (m); t = time of diffusion (s); C_o = solute concentration in the capillary, before diffusion (mol/liter); C_t = average solute concentration after t (mol/liter); and D = diffusion coefficient (m²/s).

Application of Eq. I, which is an approximated solution of Fick's second law of diffusion, results in an error of $<0.5\%$ if $D\ t/l^2 > 0.16$, which was the case in all our experiments. For accurate determinations of the solute concentration, part of the solute was labeled with ^{14}C so that its concentration could be determined by measuring the activity of the solution.

Eq. I may only be used when the following boundary conditions have been fulfilled: (a) the solute transport in the capillary takes place only by diffusion, and (b) the solute concentration at the open end of the capillary must be kept zero.

The experimental realization of these conditions is hampered by two main sources of error, which can be expressed in terms of the capillary length l. These Δl effects, reflecting sweeping-out or building-up of solution at the end of the capillary, are (a) "immersion Δl," due to rinsing of solution out of the capillary during immersion and withdrawal from the bath; and (b) "stirring Δl" as a result of too much or too little stirring in the bath to maintain zero solute concentration at the open end of the capillary.

Both effects have been discussed elaborately (5-7), but none of the authors has exactly specified the geometrical conditions. Nanis et al. (8) clearly recognized the influence of the immersion Δl effect and extensively studied both effects; however, their final conclusion still does not give a clear recommendation for optimal experimental conditions.

We used a slight modification of a method, introduced by Wang (5), in trying to eliminate the stirring Δl effect by measuring diffusion coefficients for various capillary lengths under different stirring conditions. For those conditions where the diffusivity becomes independent of l, the stirring Δl is within the experimental error.

The influence of the immersion Δl has been established by measuring at very short diffusion times so that the decrease in concentration due to diffusion is negligible. It should be stressed that, for these short diffusion times, Eq. I is not valid and, therefore, the exact solution for the diffusion equation must be used (9).

Apparatus, Procedure, and Materials

The measurements were done at 130 C under nitrogen in a jacketed vessel with a turbine impeller (6-blade, 45 mm diameter) of variable speed (6-54 rpm) in which two capillary holders each accommodating two capillaries were placed. A schematic view of the vessel is given in Figure 1. For capillaries (inner diameter 0.8 mm) of different length (10-20 mm), the position of the open end of the capillary with respect to the stirrer was always taken the same.

To avoid disturbances of the diffusion measurements by thermal convection currents arising from heating the capillaries from room temperature to 130 C, the following procedure was applied. The capillaries were placed in the solvent batch in such a position that the open ends were ca. 2 mm above the liquid surface; a total heating time of 30 min proved to be sufficient prior to the positioning of the capillaries. During heating and diffusion the bath was under 1 atm (gauge) nitrogen pressure.

As solvent we used refined groundnut oil; the solutes were either oleic or stearic acid containing a certain amount of ^{14}C-labeled acid up to a total activity of ca. 20,000 dpm (disintegrations per min)/μl. In both cases, the total acid concentration was 1 g/kg. The tracer activity was measured in a scintillation counter (Packard Tri-carb, model 3375) after dissolving the sample in 10 ml of a scintillation solution (4 g/liter of Omnifluor R in toluene).

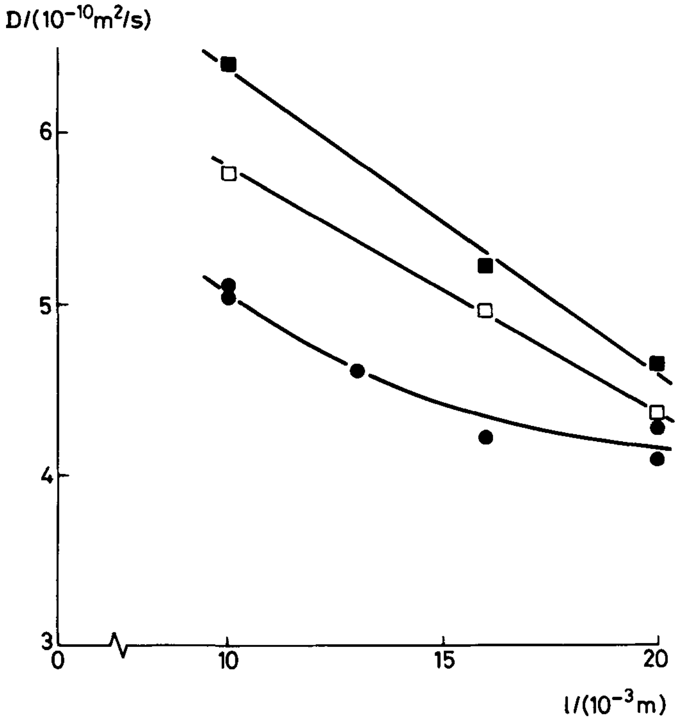

FIG. 2. Diffusion coefficient of oleic acid in groundnut oil using different capillary length and stirrer speeds; each point represents the mean of four measurements. ● = 0, □ = 10, and ■ = 30 rpm.

TABLE I

"Immersion Δl" Effect in Terms of Tracer Activity for Two Capillary Lengths[a]

Capillary length (mm)	Tracer activity (dpm) Initial	Tracer activity (dpm) After 300 s	Decrease of activity (%)
10	102478	86531	15.6
		85846	16.2
	92695	85291	8.0
		79273	14.5
20	203440	194794	4.3
		198019	2.7
	184019	181887	1.2
		175753	4.5

[a] Temp = 130 C; diffusion time = 300 s.

TABLE II

Determination of Experimental Accuracy[a]

Series number	Diffusion coefficient (10^{-10} m^2/s)	Mean diffusion coefficient of series (10^{-10} m^2/s)	Total mean diffusion coefficient (10^{-10} m^2/s)
1	3.82 3.97 3.92 3.83	3.89 (0.07)[b]	
2	3.84 3.57 3.80 3.77	3.75 (0.12)	3.84 (0.11)
3	3.80 3.94 3.84 3.99	3.89 (0.09)	

[a] Conditions: capillary length 16 mm; diffusion time 2.45 10^5 s; no stirring; stearic acid.
[b] Standard deviation in parentheses.

RESULTS AND DISCUSSION

Figure 2 shows the influences of impeller speed and capillary length on the measured diffusion coefficient for oleic acid. Measured under no stirring conditions in capillaries longer than 16 mm, the diffusion coefficient appears to be constant (ca. 4.2 10^{-10} m^2/s), which means that the Δl effects are within the experimental error. The finding that the measured diffusion coefficients for shorter capillaries under no stirring conditions are relatively higher instead of lower, which one should expect, must be explained by a rather serious immersion Δl effect. To check this, we made several measurements with very short diffusion times and without stirring. The results (Table I) indeed show that the immersion Δl effect for the short capillaries is several times stronger than that for the longer ones which is within the experimental error.

The results for stearic acid are analogous to those for oleic acid. However, the "constant" (at $l = 20$ mm) diffusion coefficient here is ca. 3.7 10^{-10} m^2/s.

The reproducibility of the method is quite good, particularly when the larger capillaries are used (Table II). At the optimal experimental conditions, i.e., 20 mm capillaries and no stirring, the standard error of the mean diffusion coefficient (95% confidence interval) was 0.16 10^{-10} and 0.23 10^{-10} m^2/s for oleic and stearic acid, respectively, the difference being due to the number of measurements.

ACKNOWLEDGMENT

J.C. Troost and J.A. Verhey skillfully executed the experiments.

REFERENCES

1. Brit. Pat. 1,101,434.
2. Ertl, H., R.K. Ghai, and F.A.L. Dullien, AIChE Journal 20:1 (1974).
3. Anderson, J.S., and K. Saddington, J. Chem. Soc., Suppl. 381 (1949).
4. Wang, J.H., J. Am. Chem. Soc. 73:510 (1951).
5. Ibid. 74:1182 (1952).
6. Gary-Bobo, C.M., and H.W. Weber, J. Phys. Chem. 73:1155 (1969).
7. Witherspoon, P.A., and D.N. Saraf, Ibid. 69:3753 (1965).
8. Nanis, L., S.R. Richards, and J.O.M. Bockris, Rev. Sci. Instr. 36:673 (1965).
9. Carslaw, H.S., and J.C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, England, 1947, p. 99.

[Received July 7, 1975]