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The Temperature Dependence of the Expansion Coefficient of Liquid Glycerides

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Abstract

The temperature dependence of the expansion per degree C, E, has been determined for a number of simple triglycerides and for natural oils and fats. This dependence could be expressed as a straight line:

$$E = E_0 + kt$$

The E-values found for simple triglycerides indicate that:

1) The E-value for the trisaturated glycerides is independent of the chain length;
2) the E-lines for triolein and the trisaturated glycerides run parallel, thus enabling the E for a mixed triglyceride as 2-oleoyl-distearoyl glycerol to be calculated from those for triolein and tristearin;
3) the E-line for trielaidin has a different slope from that of triolein.

In calculating dilatations for practical purposes, the E-values for natural oils and fats can be rounded off to 20.5 + 0.02 t.

When we have to correct for the expansion of the liquid fat phase, the equation: $U_X = E.(t_e - t_x)$ has to be changed into the more accurate expression:

$$U_X = \left[E_0 + k.\frac{t_e + t_x}{2}\right](t_e - t_x).$$

Introduction

To determine the dilatation of a fat from changes in volume between two temperatures, a number of corrections must be applied. Among these are corrections for the expansion of the glass, the sealing liquid and the liquid phase of the glyceride. In order to check the usual correction for the expansion of the liquid phase, we measured this value accurately for several pure triglycerides, as well as for many oils and fats.

When dilatation is expressed in the usual ml/g values, the small numbers which result are difficult to handle. Even the expression in ml/kg (according to practice in the U.S.A.) gives unwieldy small values. We have, therefore, used the expression more usual in Europe, in mm^3/25 g fat.

Procedures

Calculation of the Dilatation

The dilatation (1–6) is calculated from two volume readings (Fig. 1). The first reading is made at t_e degree C, a temperature at which the fat is completely liquid. A second reading is made at temperature t_x, the temperature at which the dilatation is to be determined. If these volume readings, after correction for the expansion of the glass and the sealing liquid, are V_e and V_x, respectively, then $(V_e - V_x)$ represents the increase in volume on heating from t_x to t_e degrees C. Finally the correction for the expansion, U_x, of the liquid fat at t_x, has to be made.

The dilatation can then be expressed as:

$$D_x = (V_e - V_x) - U_x \qquad [1]$$

This correction for the expansion of the liquid phase of the fat U_x can, in practice, be calculated from the equation:

$$U_x = E\ (t_e - t_x), \qquad [2]$$

where E is the expansion of the liquid phase per degree C (in mm^3/25 g), a constant.

Temperature Dependence of the Expansion per Degree C

Expansion of a liquid. The volume of a liquid on heating from 0 to t degree C is expressed as:

$$V_t = V_0\ (1 + at + bt^2 + ct^3 + \ldots .) \qquad [3]$$

The coefficient of expansion at t degree C is given by:

$$\frac{1}{V_0}\frac{dV}{dt} = a + 2\,bt + 3\,ct^2 + \ \ldots . \qquad [4]$$

Partington (7) gives for olive oil:

$a \times 10^3 = 0.68215$ ml/g degree C
$b \times 10^6 = 1.14053$ ml/g degree C
$c \times 10^8 = -0.539$ ml/g degree C
$a = 17.05$ mm^3/25 g degree C
$b = 0.06$ mm^3/25 g degree C
$c = -0.0004$ mm^3/25 g degree C

As the constant $a = 17.05$ strongly deviates from the values for the fats according to Bailey (3), and other data are not given in the literature, our measurements were carried out with pure triglycerides.

From such measurements with a number of simple triglycerides, we found that the temperature dependence of the expansion per degree C, E, can best be expressed as:

$$E = E_0 + kt \qquad [5]$$

in which:

E_0 = expansion per degree C in mm^3/25 g at t = 0C, a constant
k = slope of the line

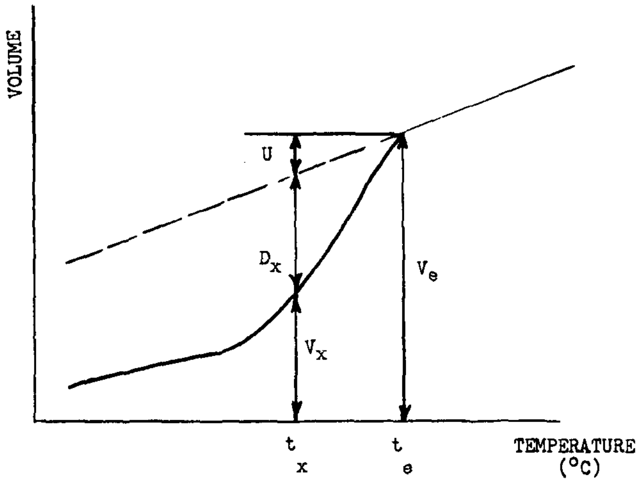

FIG. 1. $D_x = (V_e - V_x) - U_x$

Results and Discussion

The E-values for a number of triglycerides are given in Table I. These triglycerides were synthetically prepared.

It is surprising that the line for trielaidin has a slope which differs significantly from that of the cis-isomer (triolein). Since various physical constants of trielaidin, such as refractive index and density, also differ from those of the *cis*-isomer, the *trans*-configuration could be the reason for these deviations.

Equal values are found for trilaurin and tristearin, which would suggest that the expansion of the saturated triglycerides is independent of the chain length of the fatty acids. This supposition is supported by the findings of Bailey and Singleton (8).

If we assume that there is an additive relationship between these E-values, we might calculate the E-value for a mixed glyceride. For example, 2-oleoyl-distearoyl glycerol would give a value of $20.5 + 0.027$ t viz. $\frac{1}{3} \times 20.1 + \frac{2}{3} \times 20.7 + 0.027$ t.

Since we did not experiment with mixed glycerides, the only possibility to test this assumption is by comparing the results with those given by Landman et al. (9) for 2-oleoyl-palmitoyl-stearoyl glycerol and 2-oleoyl-distearoyl glycerol (Table II).

With $20.5 + 0.027$ t we calculate for $E = 21.9$ mm^3/25 g at ca. 50C, which is in fairly good agreement with the values given by Landman et al. (9).

The temperature dependence of the expansion per degree C has also been determined for a number of natural and hardened oils and fats.

Statistical analysis of all the numerical data available for oils and fats resulted in the general expression:

$$E = 20.5 + 0.0187\ t \qquad [6]$$

TABLE I

Temperature Dependence of the Expansion of Some Single Triglycerides *in the Liquid State*

Triglyceride	Expansion per C mm^3/25 g $E = E_o + kt$
Trilaurin	20.7 + 0.027 t
Tristearin	20.7 + 0.027 t
Triolein	20.1 + 0.027 t
Trielaidin	20.9 + 0.015 t
Trilinolein	19.2 + 0.027 t

TABLE II

Expansion per Degree C of 2-Oleoyl-palmitoyl-stearoyl Glycerol (POS) and 2-Oleoyl-distearoyl Glycerol (SOS)

Triglyceride	Temp range	ml/kg	mm^3/25 g
POS	37–63 degree C	0.883	22.1
SOS	42–63 degree C	0.873	21.8

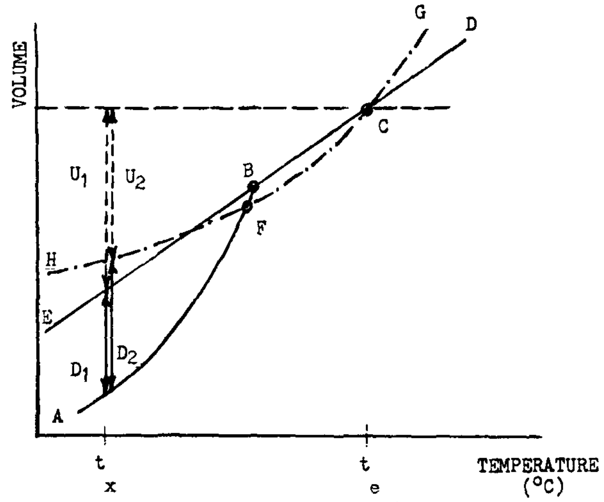

FIG. 2. $U_2 = \left[E_o + k.\frac{t_e + t_x}{2}\right](t_e - t_x)$

$U_1 = E\ (t_e - t_x)$

$U_2 > U_1$

This value being rounded off to $E = 20.5 + 0.02$ t may be used for all fats when measuring their dilatations for practical purposes.

Standard deviation of the slope $(k) = 0.005$; the constant E has a confidence interval of 95% between the values 20.5 ± 0.5. In consequence of the temperature dependence of the expansion per degree C, the correction U_x must now be calculated by integrating E to t throughout the temperature range t_x to t_e.

$$U_x = \int_{t_x}^{t_e} E\ dt \qquad [7]$$

or, substituting $E_o + kt$ for E

$$U_x = \int_{t_x}^{t_e} (E_o + kt)\ dt$$

$$U_x = (t_e - t_x)\left[E_o + k.\frac{t_e + t_x}{2}\right] \qquad [8]$$

In the V/t diagram, Figure 2, the dilatation D_1 is calculated using the correction $U_1 = E\ (t_e - t_x)$, in which $E =$constant (line EBD), and the dilatation D_2, using the correction $U_2 = \int_{t_x}^{t_e} E\ dt$, in which $E = E_o + kt$ (line HFG). The difference between D_1 and D_2, especially at extremely low temperatures <-30C is here clearly seen.

Within the most generally applicable temperature range: $t_x = 0$–60C, the use of the correct expression for E ($E = E_o + kt$) gives dilatations which are only 10 units higher. In practice this is of no importance.

At temperatures within the range: $t_x = 0$ to -60C, the use of the correct expression for E results in dilatations which are 30–70 units higher. Corrections of this order cannot be neglected.

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