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Temperature and storage age (weekly basis)-dependence of olive oil viscosity

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ABSTRACT

The dynamic viscosity of olive oil samples of different storage ages in weekly basis from different locations was measured as a function of temperature. In this study, the dynamic viscosity as a function of storage age in weekly basis decreases with increasing temperatures. Three and multi-constant formulas were proposed to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples. The best AAD% was calculated using our proposed formulas to be 0%.

KEYWORDS

Acidity;
Storage ages;
Olive oil;
Fitting equations.

INTRODUCTION

Viscosity is a fundamental characteristic property of all liquids and it is one of the most important parameters required in the design of technological processes.

There were numerous researchers who worked to propose alternative equations to describe the effect of temperature on dynamic viscosity. An equation to replace the well-known Arrhenius-type relationship was derived by Giap tested his model using six vegetable oils and proved its accuracy[1]. Barnett proposed a functional form for the variation of liquid viscosity (η) in cP with temperature (t) in °C[2]. De Guzman suggested three-constant form to represent liquid viscosity as a function of temperature[3]. Vogel also proposed a three-constant representation[4]. Reid represented liquid viscosity in the polynomial form[5]. Daubert utilized a new formula to represent the dynamic viscosity data as a function of temperature for a large number of substances[6]. Abramovic described the effect of temperature on dynamic viscosities for a number of vegetable oils by using modified versions of the Andrade equation[7]. In addition, Abramovic suggested a new form to describe the effect of temperature on viscosity which as been also used by several investigators[8-10].

The main goal of this work is to study the dependence of dynamic viscosity of olive oil on temperature. The relationship between the dynamic viscosity of olive oil with temperature and storage age will be found by fitting equations.

THEORY

Viscosity is a measure of the resistance to flow or shear. Viscosity can also be termed as a drag force and is a measurement of the frictional properties of the fluid. It can be expressed in two distinct forms:

1. Dynamic viscosity (η)

2. Kinematic viscosity (ν)

Dynamic viscosity is defined as the ratio of shear stress (force over cross section area) to the rate of deformation (the difference of velocity over a sheared distance), and it is presented as:

$$\eta = \frac{\tau}{\frac{\partial u}{\partial x}} \quad (1)$$

Where, η is the dynamic viscosity in Pascal-second (Pa.s); τ is shear stress (N/m^2); and, $\frac{\partial u}{\partial x} = \gamma$ is rate of deformation or velocity gradient or better known as shear rate (1/s)[11].

The Kinematic viscosity requires knowledge of mass density of the liquid (ρ) at that temperature and pressure. It is defined as:

$$\nu = \frac{\eta}{\rho} \quad (2)$$

Where, ν is kinematic viscosity in centistokes (cSt), ρ is in g/cm^3[11].

Simple as well as complex expressions have been proposed for the representation of liquid viscosity as a function of temperature with the main objective of representing the available experimental data.

Among several proposed relations, De Guzman proposed the simplest form of representation of liquid dynamic viscosity as a function of temperature[3,7], which is:

$$\nu = \frac{\eta}{\rho} \quad (4)$$

Abramovic described the effect of temperature on dynamic viscosity by using the following equations:

$$Log\,\eta = \frac{A}{T} - B \quad (5)$$

$$\eta = A - BLogt \quad (6)$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin, t is the temperature in degrees Celsius. A and B in equations 4, 5 and 6 equations are constants. The constants of equations (5) and (6) of olive oil and other oils are presented by Abramovic[8].

Abramovic used the Andrade equations of three-constant formula that are represented in the following equations:

$$Ln\eta = A + \frac{B}{T} + \frac{C}{T^2} \quad (7)$$

$$Ln\eta = A + \frac{B}{T} + CT \quad (8)$$

Another study by Natarajan utilized the Antoine type equation given by:

$$Log\,\eta = \frac{B}{C - T} + A \quad (9)$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin. A, B and C are constants. The constants of Andrade equations of olive oil and other oils are presented by Abramovic[7,8]. The constants of equation (9) for dynamic viscosity (η) of olive oil and some liquids are given[12,13].

A study by Reid represented liquid dynamic viscosity in the polynomial form:

$$Ln\eta = A + \frac{B}{T} + CT + DT^2 \quad (10)$$

Where η is the dynamic viscosity in cP and T is the temperature in Kelvin. A, B, C and D are constants. Reid in his work estimated the constants of equation (10) for several substances[5].

EXPRIMENTAL

The viscosity of olive oil samples of crop 2010 from two different locations (AL yamun (L_3) and Beta (L_4)) at different temperature was measured weekly during the period from June 2011 till August 2011. The experimental data were fitted and the correlation constants of the best fits were estimated.

Experimental apparatus

Two models of viscometer of different ranges were used to measure the range of viscosity of olive oils samples: Low viscosity readings of olive oil samples were measured using the Digital Viscometer Model NDJ-8S with accuracy $\pm$ 1%. A Brookfield Viscometer Model DV-I+ with accuracy $\pm$ 1% also was used to measure the viscosity of olive oil samples. The SP-1 spindle was operated at 60 rpm. The calibration of the Brookfield Viscometer Model DV-I+ was verified by using standard fluid with a viscosity of 4840 cP with accuracy ± 1% at room temperature and RV-3 Spindle at 2 rpm was used[14].

Temperature was measured using Digital Prima Long Thermometer with accuracy ±1% which measures temperature ranges from –20°C up to +100°C.

The Fried Electric model WB-23 was used to increase the temperature of the oil samples to a specific temperature.

Statistical analysis

Some empirical relations were found to describe the temperature dependence of dynamic viscosity by using SPS program. The correlation constants for the best fit were estimated. The best fit equation was chosen based on the percentage of average absolute deviation (%AAD) and standard deviation (SD) of the data[11].

EXPERIMENTAL RESULTS AND DISCUSION

Temperature-dependence of dynamic viscosity

The dynamic viscosity of olive oil samples from two different locations (L_3 and L_4) as a function of temperature, which was measured after some weeks, is plotted in Figure 1 a and b.

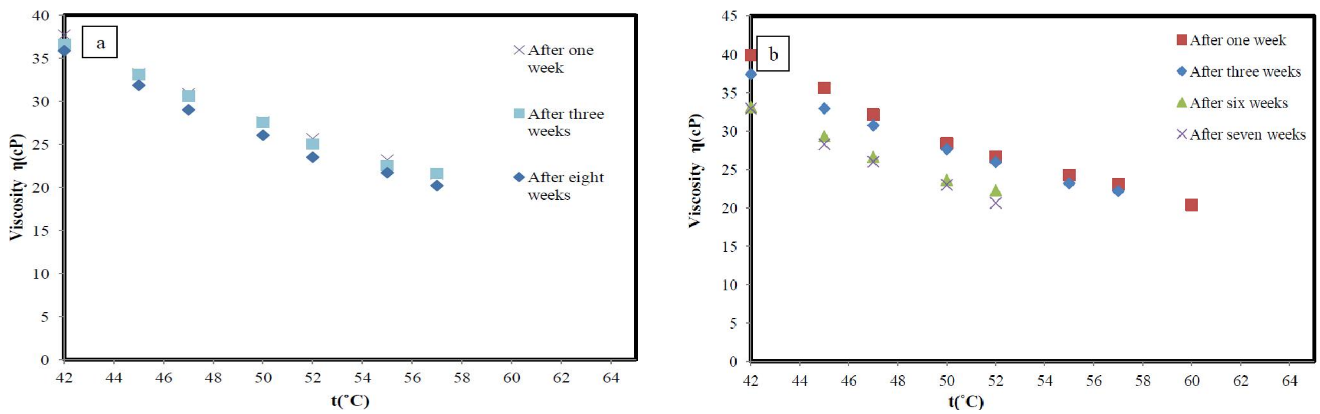

Figure 1 : The measured values of the dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 for different storage age in weeks as a function of temperature.

A comparison was made between the measured experimental data of dynamic viscosity (η_{exp}) and the previously calculated values (η_{cal}). The calculated values found by two-constant formula of Abramovic's $\eta = A - BLogt$ and three-constant formula of Andrade's $Ln\eta = A + \frac{B}{T} + CT$. A, B and C are constants for olive oil. It was found that the literature values didn't fit our experimental dataUsing Abramovic's and Andrade's formulas, the AAD% values were found by this work to be from 3.1% to 12.4% and from 0.8% to 15.8% respectively. As a result, their formulas were not the best fit for our experimental data of dynamic viscosity of olive oil samples. Accordingly, a modification was introduced to their formula in order to obtain a suitable description of our experimental data of dynamic viscosity as a function of temperature. The constants of Abramovic's and Andrade's formulas were determined using the modification. Our experimental values (η_{exp}) and calculated values (η_{cal}), using the modified form of Abramovic's and Andrade's formulas of dynamic viscosity at different temperatures are given. TABLES 1 and 2 tabulate AAD% and SD values. TABLE 1 shows AAD% ≤ 1.8%. TABLE 2 shows AAD% ≤ 1.6%. The results indicate that the modified form of Abramovic's and Andrade's formulas didn't fit exactly our experimental data. The values of the constants of the modified form of Abramovic's and Andrade's formulas in TABLES 1 and 2 are in disagreement with Abramovic's values (TABLE 3). This is might be due to free fatty acid composition of different olive oil samples.

Three and multi-constant formulas were proposed by this work to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples. The η_{exp} and η_{cal} were used to propose the formulas that fit our experimental data. That is, AAD% and

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TABLE 1 : Our values of A, B, AAD% and SD using the modified Abramovic's formula of two-constant of olive oil samples from L_3 and L_4.

Location	Storage age (week)	A (cP)	B (cP)	Temp.Range (°C)	AAD%	SD (cP)
L_3	1	231.5	119.5513	42.0 – 57.0	1.5	0.5
	3	231.2	119.6388	42.0 – 57.0	1.3	0.5
	8	228.0	118.4390	42.0 – 57.0	1.7	0.7
L_4	1	241.3	124.4046	42.0 – 60.0	1.6	0.9
	3	222.2	114.0817	42.0 – 57.0	1.4	0.6
	6	225.0	118.6790	42.0 – 55.0	1.8	0.6
	7	243.0	129.4211	42.0 – 55.0	1.5	0.5

TABLE 2 : Our values of A, B, AAD% and SD using the modified Andrade's formula of three-constant of olive oil samples from L_3 and L_4.

Location	Storage age (weeks)	A	B (K)	C (K^2) × 10^{-5}	Temp. Range (K)	AAD%	SD
L_3	1	-3.64	3050.001	-771	315.0 – 330.0	0.9	0.3
	3	-3.60	3052.000	-785	315.0 – 330.0	0.6	0.3
	8	-3.00	3050.289	-984	315.0 – 330.0	0.7	0.4
L_4	1	-3.31	3050.287	-858	315.0 – 333.0	0.7	0.5
	3	-4.14	3050.281	-618	315.0 – 330.0	1.6	0.5
	6	-2.60	3050.291	-1142	315.0 – 325.0	1.4	0.4
	7	-1.13	3050.299	-1612	315.0 – 325.0	1.5	0.4

TABLE 3 : The constants given by Abramovic using Abramovic's and Andrade's formulas.

Equation	A	B	C	Temperature range (K)
Abramovic'sformula	235.40 cP	124.10 cP	-	298.15to 328.15
Andrade's formula	-32.72	7462.27 K	0.04 1/K	

SD values are chosen to select the suitable prediction.

If two-constant formula is proposed the fitting curves will not be in good agreement with the experimental data. Accordingly, the two-constant formula is not suitable for our experimental data where the AAD% gives very high value.

It was found that our proposed formula of three-constant $\eta = A - BLogt$ and multi-constant $Ln\eta = A + \frac{B}{T} + CT$ fit our experimental data of dynamic viscosity. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in TABLES 4 and 5. TABLES 4 and 5 show AAD% ≤ 0.2%; therefore, our proposed two and multi-constant formulas are more suitable to describe the temperature dependence of dynamic viscosity of olive oil samples.

TABLE 4 : Our values of A, B, C, AAD% and SD using our proposed three-constant formula of olive oil samples of L_3 and L_4.

Location	Storage age (weeks)	A	B (K)	C (K)	Temp.Range (K)	AAD%	SD (cP)
L_3	1	-7.30653	-3053.11	-35.6963	315.0 – 330.0	0.0	0.1
	3	-7.25578	-3053.05	-33.9289	315.0 – 330.0	0.0	0.3
	8	-7.62857	-3053.43	-42.5131	315.0 – 330.0	0.0	0.3
L_4	1	-7.36674	-3053.25	-38.5983	315.0 – 333.0	0.1	0.4
	3	-7.04828	-3052.78	-28.6302	315.0 – 330.0	0.0	0.2
	6	-7.87487	-3053.66	-46.5050	315.0 – 325.0	0.0	0.2
	7	-8.57047	-3054.37	-61.7518	315.0 – 325.0	0.0	0.2

Figure 2 a and b and 3 a and b show our experimental data and our fitting curves using our proposed three and multi-constant formulas of dynamic viscosity of olive oil samples from two different locations (L_3 and

L_4) of different storage ages as a function of temperature.

TABLE 5 : Our values of A, B, C, D, E, AAD% and SD using our proposed multi-constants formula.

Location	Storage age (week)	A (cP)	B (cP.°C)	C (cP)	D (cP/°C^E)	E	TempRange (°C)	AAD%	SD (cP)
L_3	1	-150.31904	3820.695	25.94402	694.2263	-2624.33	42.0 – 57.0	0.0	0.1
	3	41.22569	1897.006	-13.18860	694.2263	-2624.33	42.0 – 57.0	0.0	0.4
	8	-299.88700	5270.429	56.30426	694.2263	-2624.33	42.0 – 57.0	0.0	0.2
L_4	1	-355.97400	6073.650	67.27800	694.2263	-2624.33	42.0 – 60.0	0.2	0.3
	3	-229.89000	4514.184	42.72617	694.2263	-2624.33	42.0 – 57.0	0.0	0.1
	6	-1134.18000	13876.920	225.60200	694.2263	-2624.33	42.0 – 55.0	0.0	0.4
	7	-1116.07000	13878.850	220.74040	694.2263	-2624.33	42.0 – 55.0	0.0	0.6

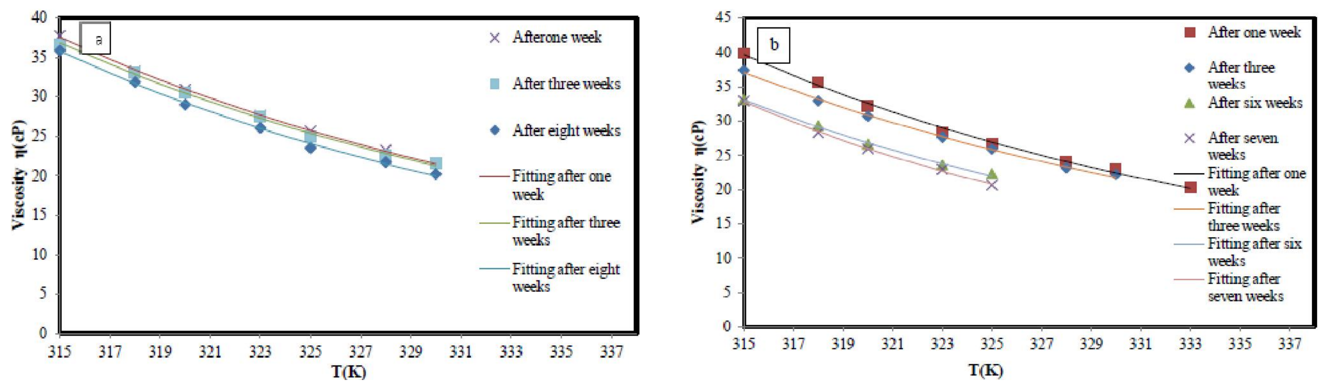

Figure 2: The dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 of different storage ages as function of temperature. The solid lines are representing our proposed three-constant formula and the points are representing our experimental data.

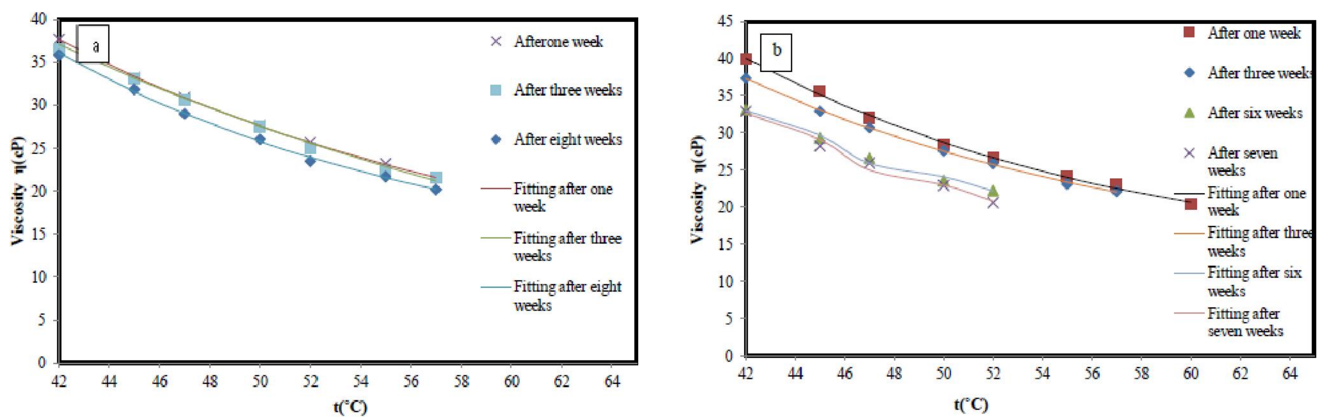

Figure 3: The dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 of different storage ages as function of temperature. The solid lines are representing our proposed multi-constant formula and the points are representing our experimental data.

Storage age-dependence of dynamic viscosity

The dynamic viscosity of olive oil samples from two locations (L_3 and L_4) was measured as a function of storage age in weeks at 47ºC as shown in Figure 4.

The experimental values of the dynamic viscosity of olive oil samples from L_3 and L_4 of different storage ages were fitted by using our multi-constant formula. Our multi-constant formula is proposed to be:

$$\eta = At^2 + Bt + C + De^{Et} \tag{11}$$

Where η is the dynamic viscosity in cP, t is the storage age in weeks, A, B, C, D and E are constants. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in TABLE 6. TABLE 6 shows that

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AAD% = 0%; therefore, our proposed multi-constant formula are suitable to describe the storage age dependence of dynamic viscosity of olive oil sample.

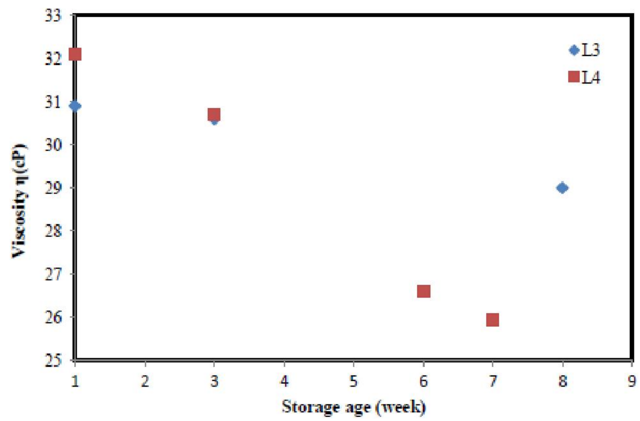

Figure 4: The measured values of dynamic viscosity of olive oil samples from $L_3$and L_4 of as function of storage age in weeks.

TABLE 6 :Our values of A, B, C, D and E, AAD% and SD using our proposed formula.

The location	A (cP/week^2)	B (cP/week)	C (cP)	D (cP)	E	AAD%	SD
L_3	-0.118	1.469	23.846	7.378	-0.257	0.0	0.0
L_4	0.207	-3.300	38.930	-16.197	-1.466	0.0	0.0

Figure 5 shows our experimental data and our fitting curves using equation 11 of dynamic viscosity of olive oil samples from L_3 and L_4 as a function of storage age in weeks.

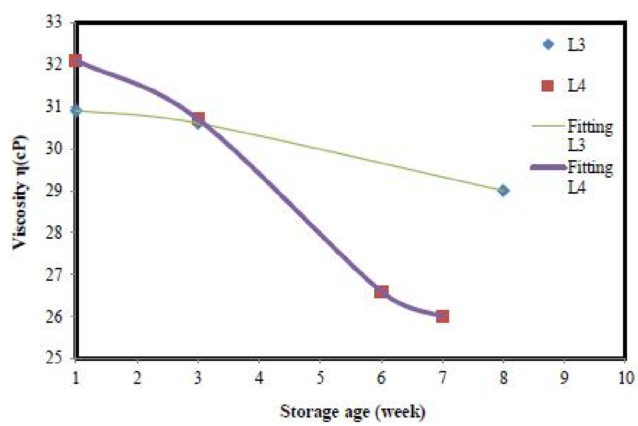

Figure 5: The dynamic viscosity of olive oil samples from L_3 and L_4 as a function of storage age in weeks. The solid lines are representing equation 11 and the points are representing our experimental data.

CONCLUSION

The effect of dynamic viscosity as a function of storage age in weeks at 42°C showed that for location L_3 η = 37.7 cP (1-week storage age) and η =35.85 cP (8-week storage age) and for location L_4 η = 39.9 cP (1-week storage age) and 32.9 cP (7-week storage age). The dynamic viscosity results of weekly basis in this study indicate that the dynamic viscosity of olive oil samples decreases as a function of storage age in weeks. The dynamic viscosity of olive oil decreased as a function of storage age at a greater rate in samples from L_4 than in those of L_3.

All experimental measurements of dynamic viscosity of olive oil samples of different locations in Palestine give values which slightly differ from one location to another. The difference might be due to different parameters that influence on the fatty acid composition of olive oil. The fatty acid composition of olive oil varies widely depending on the cultivator, maturity of the fruit, altitude and climate. Hot climate affects the fatty acid composition of olive oils[11,15-17]. The cooler regions will yield oil with higher oleic acid than warmer climates; therefore, a cool region olive oil may be more monounsaturated in content than warm region oil[11].

The dynamic viscosity values of olive oil sample of crop 2010 from L_4: η = 39.9 cP (1 week storage age) are greater than the values from L_3: η = 37.7 cP (1week storage age). The altitude of location L_3 is 140 – 230 m while the amount of rain was 514 mm. The altitude of location L_4 is 520 – 600 m and the amount of rain of location was 333.2 mm[18]. This information gives a reasonable cause that justifies the slight difference in dynamic viscosity values of olive oil from L_3 and L_4.

The measured experimental results of dynamic viscosity of olive oil samples are compared against the previously calculated values found by Abramovic's formula of two-constant $\eta = A - BLogt$ and Andrade's formula of three-constant $Ln\eta = A + \frac{B}{T} + CT$ for olive oil. For instance, the calculated values of dynamic viscosity at 45°C were found to be 30.2 cP and 32.0 cP, respectively. Our measured experimental value at 45°C (36.6cP) shows significant difference between our result and the literature value. This indicates that Abramovic's and Andrade's formulas are not the best fit to be used for our experimental data of dynamic viscosity of olive oil samples. Abramovic's and Andrade's formulas were modified to fit our experimental values. As a result of this modification, the constants A, B and C were determined using Abramovic's and Andrade's formulas. The calculated dynamic viscosity using the modified form of Abramovic's and Andrade's formulas at 45°C were found to be 38.5 cP and 37.6 cP, respectively, which indicate that Abramovic's and Andrade's modified formulas don not fit exactly our experimental data. Three ($Ln\eta = A - \frac{B}{T + C}$) and multi ($\eta = A + \frac{B}{t} + CLn(t) + Dt^{E}$) -constant formulas are proposed to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples in our regions. The constants of our proposed formulas were estimated to give the best fit.

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