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THERMAL PROPERTIES OF JOJOBA WAX

I. CRYSTALLIZATION BEHAVIOUR

V. GONZÁLEZ-GONZÁLEZ, R. O. VALERO-COSS and E. CAMPOS-LÓPEZ

Centro de Investigación en Química Aplicada Saltillo, Coahuila, México

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The thermal behaviour of Jojoba (Simmondsia chinensis) liquid wax was studied by differential scanning calorimetry (DSC), varying the annealing conditions. The fusion enthalpy (ΔHf) of the unannealed material was 27.1 cal/g; the relationship between heat capacity (Cp) and temperature could be expressed by the following equation: $Cp = 9.51 \times 10^{-4}\, T + 0.129$. It was found that Jojoba wax presents four endothermic transitions (α, β, γ and δ) including fusion α, estimable at low heating rates (1 K/min); the activation energies (Ea) for transitions α and γ were 51.18 and 64.82 Kcal/mole respectively; and it was observed that the transition temperatures α and γ maintained a lineal relationship with the square root of the heating rate (Hr).

Jojoba (Simmondsia chinensis) wax has very similar properties to whale oil and in recent years has become a potential substitute for this oil [1]. Apart from this specific interest, the need to find new crops from arid zones has attracted attention to Jojoba as an important potential renewable source of raw materials [2, 3].

The wax, liquid at room temperature, represents about 50% by weight of the Jojoba seed. Its chemical composition is made up of 80% lineal esters, coming from eicos-11-enoic, docos-13-enoic acids and eicos-11-enol and docos-13-enol alcohols [4, 5]. The chemical structure of these esters allows the use of their functionality to prepare different derivatives with probable industrial uses.

In spite of the numerous papers published, the thermal properties of the original wax have not been approached in depth, to date. Although Miwa [6] previously reported a value of 21 cal/g for the fusion enthalpy (ΔHf), studies have not been exhaustive enough to give a complete picture of the thermal behaviour of this material, which also includes the heat capacity (Cp), and crystalline behaviour, which has only been studied by X-ray in the hydrogenated wax [7].

Using differential scanning calorimetry (DSC) it is not only possible to determine the heat that accompanies the physical processes (melting, crystallization, etc.) being tested, but also a deeper study of its kinetic characteristics can be made. Different authors have developed mathematical models for handling experimental calorimetric data in the calculation of kinetic parameters such as activation energy (Ea) and rate constants (k).

Experimentally, there are two alternatives for using calorimetry in kinetic studies, the isothermic [8] and dynamic [9] modes: The first presupposes determination, at the same temperature, of the heat evolved by the process at different times (t)

and the application of this data in the calculation of the rate constants (k) and activation energies. The dynamic mode requires study of the process at different heating or cooling rates (Hr and Cr respectively) and presupposes a semi-logarythmic relationship between this rate and the temperature at which the reaction is being done, which could be represented by the equation:

$$\ln Cr = C + Ea/RTm \qquad (1)$$

where Cr is the cooling rate (or heating rate) in K/min; Tm the peak temperature in K; Ea the activation energy in Kcal/mole R the universal gas constant; and C an adimensional constant. In this way it is possible to calculate the activation energy of the process by determining maximum peak temperatures (Tm) at different heating or cooling rates (Hr or Cr) and tracing a straight line between $1/Tm$ *vs.* ln (Hr or Cr) whose slope will be proportional to Ea.

Experimental

Materials

The Jojoba wax used was supplied by the Scientific and Technological Research Center of the University of Sonora (CICTUS) and was mechanically extracted from the seed and filtered to eliminate insoluble impurities. The composition of this wax has already been reported by other authors [4, 5].

Thermal analysis

The instrument used in these studies was a Dupont 990 thermal analyzer adapted with a differential scanning calorimeter of the same brand. Calorimetry calibration was carried out periodically using synthetic sapphire for the quantative determinations of ΔHf and Cp, temperatures were corrected using indium, mercury, zinc and tin standards. To avoid the presence of a reactive atmosphere, pure nitrogen was used as a dynamic inert atmosphere, maintained at a flux of 100 ml/min. Depending on the type of experiment the sensitivity (Δqs), the heating or cooling rate (Hr or Cr respectively) and the mass (m), of the sample were varied; the conditions used are described in the text. The samples were taken with a micro-syringe and placed in aluminum pans where their mass was determined gravimetrically.

Determination of heat capacity (Cp)

Heat capacities, Cp, were determined only in the liquid state, the temperature range studied was 300 – 420 K, the masses of the samples varied between 1.0 and 1.6 mg. The heating rate (Hr) of 20 K/min remained constant during all the runs. The quantitative heat determination comprised of the endotherms was calculated by means of the following Eq. [10]:

$$\Delta H = \frac{60A\ Hr\ E\ \Delta qs}{m} \qquad (2)$$

where ΔH are the calories, m is the mass in grams, A the area below the curve in square inches and Δqs the sensitivity in calories/second-inch.

Enthalpy of melting

The fusion enthalpy, ΔH, was measured in amorphous material (unannealed) with a mass of 1.8 mg and heating rate of 20 K/min, by means of Eq. (2).

Melting and crystallization

To induce crystallization the material was subjected to a temperature of 275 K at annealing times that fluctuated between 0 and 60 min.

The activation energies corresponding to transitions α and γ were determined by heating the material to 343 K and cooling it at different rates (Cr) which varied between 2–30 K/min, determining the maximum temperature (Tm) of the exotherm.

Results and discussion

In Table 1 the values obtained for the heat capacities are shown and the standard deviations observed are indicated in one of the columns, based on an average of five determinations. The same values are shown in graphic form in Fig. 1 where the lineal relationship between heat capacity (Cp) of Jojoba liquid wax and in the

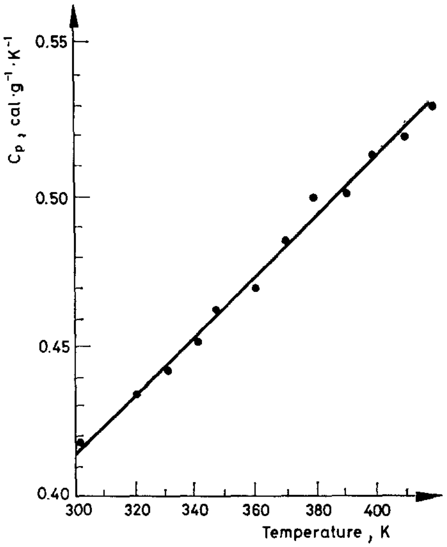

Fig. 1. Heat capacity (Cp) of liquid Jojoba wax between 300–420 K

Table 1

Heat capacities of jojoba liquid wax obtained with different temperature ranges, showing standard deviations

T, °C	Cp cal/g °C	Standard deviation
300	0.4180	0.106
310	0.4239	0.018
320	0.4342	0.016
330	0.4420	0.017
340	0.4529	0.015
350	0.4614	0.013
360	0.4690	0.015
370	0.4797	0.012
380	0.4923	0.019
390	0.5018	0.015
400	0.5123	0.018
410	0.5189	0.018
420	0.5923	0.017

300–420 K temperature range, can be seen. Dependence of the heat capacity (Cp) on the temperature can be expressed by the following equation:

$$Cp = 9.51 \times 10^{-4} \mathrm{I} + 0.129 \tag{3}$$

In Fig. 2 the endotherms obtained at different annealing times (0–60 min) at 275 K are shown; from the first endotherm (corresponding to 0 annealing time)

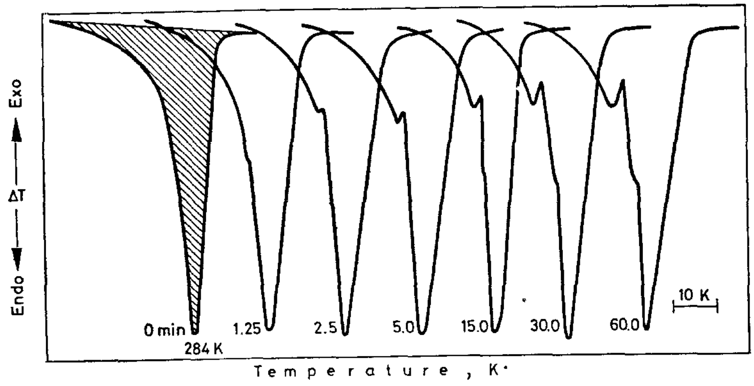

Fig. 2. Endotherm corresponding to the solid-liquid transition, showing the influence of annealing time at 275 K and maintaining a constant heating rate (Hr)

and using equation 2, the fusion enthalpy (ΔHf) was calculated and found to be 27.1 cal/g.

The annealing effect can be appreciated in the endotherms shown there. The appearance of an additional endotherm can be seen and becomes more noticeable when the annealing time is increased; another additional endotherm can also be seen in the form of a small shoulder in the lower temperature part of the main endotherm. Figure 3 shows the endotherm obtained at a heating rate of 1 K/min. Besides the two endotherms (α and γ) already mentioned, two other transitions can be seen, making a total of four, named in Figs 3 as α, β, γ and δ, and an exotherm at the end of the fusion, the presence of which could be due to the heat

Table 2

Crystallization temperatures and heating rate, showing corresponding crystallization temperatures

Transition α			Transition γ		
Cr, °C/min	*T*max, K	$1/T$ K$^{-1}\cdot 10^3$	*Cr*, °C/min	*T*max, K	$1/T$max K$^{-1}\cdot 10^3$
2	273+ 1.7	3.6383	2	273+ −10.7	3.8102
5	273+ −0.6	3.6690	5	273+ −12.0	3.8292
8	273+ −1.7	3.6839	8	273+ −12.8	3.8409
10	273+ −1.9	3.6866	10	273+ −13.0	3.8439
15	273+ −4.0	3.7154	15	273+ −14.5	3.8662
20	273+ −4.3	3.7195	20	273+ −15.0	3.8737
30	273+ −6.0	3.7432	30	273+ −16.1	3.8902

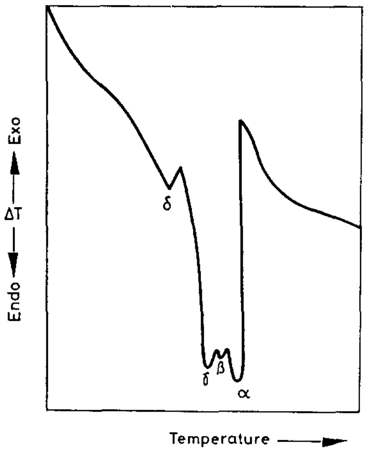

Fig. 3. Endotherms showing the appearance of additional transitions α, β, γ and δ as a consequence of low heating rate (*Hr*) (1 K/min)

dissolution of small incompatible microphases, a phenomena previously found in polymorphic studies of fat mixtures [11].

The crystallization exotherms obtained at different cooling rates are shown in Fig. 4; these determinations were carried out by heating the material to 343 K and maintaining that temperature for quarter of an hour to achieve homogeneity and then cooling it at rates varying between 2–30 K/min. Whilst the cooling rate is lower additional exotherms are seen to appear and the displacement of maximum transition temperatures (*Tm*) can also be appreciated simultaneously with a broadening of the exotherm. The numerical data of heating rates, maximum temperatures (*Tm*) and corresponding inverse values (1/*Tm*), are shown in Table 2; the drawing in Fig. 5 was traced from this data and the lineal relationship between 1/*Tm* and log *Cr* can be seen. Using Eq. (1) the activation energies were calculated and found to be 51.1 and 64.8 Kcal/mole (Table 3) for the transitions α and γ respectively.

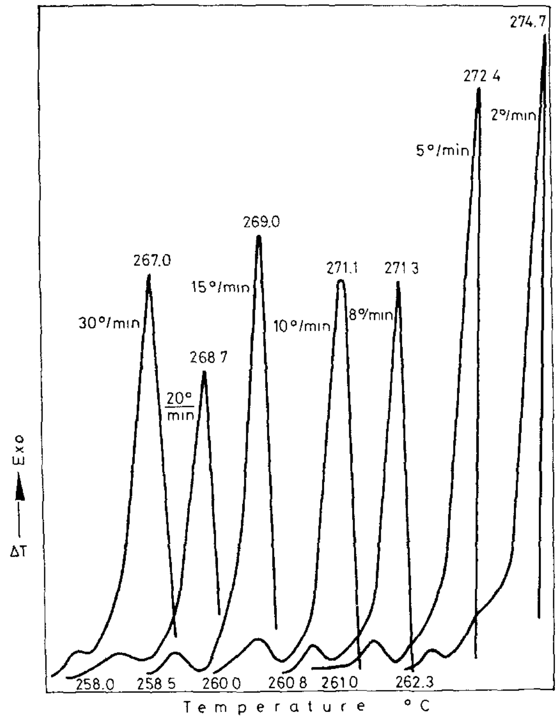

Fig. 4. Exotherms corresponding to the liquid-solid transition, showing the solidification exotherm at different cooling rates from which the activation energies were calculated

Finally, in Fig. 6 the lineal dependence between the square root of *Cr* and *Ti* is presented as well as the extrapolation at $Cr = 0$, from which the values 277 K

Table 3

Activation energies of jojoba wax calculated for the transitions α and γ, using both the initial and maximum temperatures

Transitions	*Ea*, Kcal/mole
α Solid-liquid	51.1
γ Solid-solid	64.8

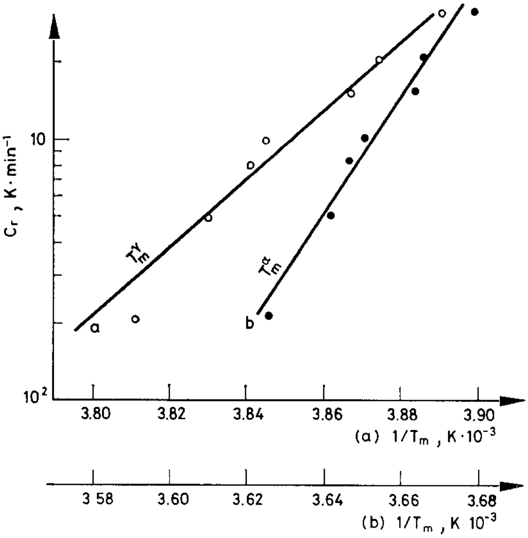

Fig. 5. Semi-logarythmic drawing, between the heating rate and crystallization temperature from whose slope the activation energy is calculated

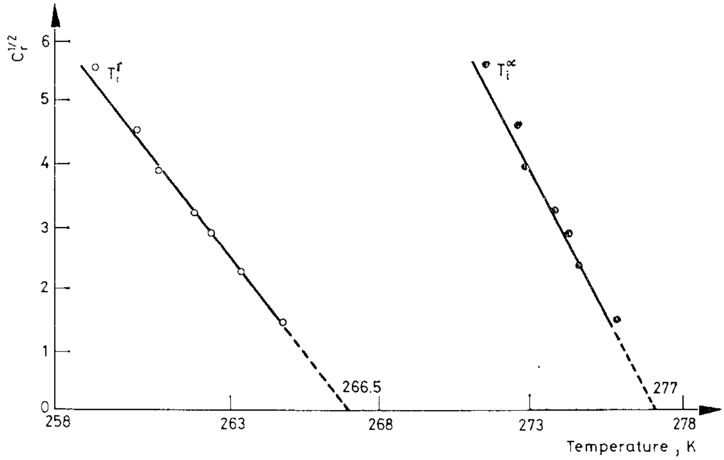

Fig. 6. Lineal relationship between the square root of the temperature, showing the extrapolation at cooling rate = 0, from which the true value of the corresponding transition temperature is obtained

and 266.5 K for the transitions α and γ respectively, were obtained, values which represent the real temperatures when the effect of the heating rate [12] is eliminated.

Conclusions

Heat capacities of Jojoba wax in its liquid state (300–420 K) were determined showing a temperature dependence which can be expressed by the following equation:

$$Cp = 9.51 \times 10^{-4} T + 0.129\,.$$

Jojoba wax presents a polymorphic behaviour giving four endotherms only noticeable at low heating rates (Hr = 1 K/min) and high annealing times (60 min) at 275 K/min.

Activation energies obtained at different cooling rates (Cr) and using the dynamic model were found to be 64.8 and 51.1 Kcal/mole for the transitions γ and α respectively.

The maximum temperatures of the endotherms (α and γ) show a lineal relationship with $Cr^{1/2}$ and the values of Ti observed by extrapolation at $Cr = 0$ were found to be $Ti^{\alpha} = 277$ K and $Ti^{\gamma} = 266.5$ K.

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Résumé — Le comportement thermique de la cire liquide de Jojoba (Simmondsia chinensis) a été étudié par analyse calorimétrique différentielle (DSC) en faisant varier les conditions de recuit. L'enthapie de fusion (ΔH_f) de l'échantillon non recuit est de 27,12 cal/g; le rapport entre la chaleur spécifique (C_p) et la température a pu être exprimé par l'équation suivante: $C_p = 9.51\times 10^{-4}\,T + 0.129$. On a trouvé que la cire de Jojoba présente quatre transitions endothermiques (α, β, γ et δ) en incluant la fusion α, décelable aux faibles vitesses de chauffage (1°/min); les énergies d'activation respectives (E_{ac}) se sont élevées à 51.18 et 64.82 kcal/mol pour les transtions α et γ sont en relation linéaire avec la racine carrée de la vitesse de chauffage (H_r).

Zusammenfassung — Das thermische Verhalten des flüßigen Wachses von Jojoba (Simmondsia chinensis) wurde durch Differential-Abtastkalorimetrie (DSC) unter Änderung der Wärmebehandlungsbedingungen untersucht. Die Schmelzenthalpie (ΔHf) des unbehandelten Materials betrug 27.12 cal/g; der Zusammenhang zwischen der Wärmekapazität (C_p) und der Temperatur konnte durch folgende Gleichung ausgedrückt werden: $Cp = 9.51\times 10^{-4}\,T + 0.129$. Es wurde festgestellt, daß das Jojoba-Wachs vier endotherme Übergänge (α, β, γ und δ) aufweist, darunter die Schmelze α, die bei niedrigen Aufheizgeschwindigkeiten zu ermitteln ist (1°K/min); die Aktivierungsenergien (Eac) für die Übergänge α und γ betrugen 51.18 bzw. 64.82 Kcal/mol. Es wurde beobachtet, daß die Übergangstemperaturen α und γ in linearem Zusammenhang mit der Quadratwurzel der Aufheizgeschwindigkeit (Hr) waren.

Резюме — Изучено термическое поведение жидкого воска Jojoba (Simmondsia chinensis) с помощью дифференциальной сканирующей калориметрии (ДСК), варьируя условия аннелирования. Энтальпия плавления неаннеиброванного материала составляла 27.12 кал/г. Связь между теплоемкостью (C_p) и температурой может быть выражена уравнением: $Cp = 9.51\times 10^{-4}T + 0.129$. Найдено, что воск Jojoba показывает четыре эндотермических перехода (α, β, γ и δ), включая плавление α, обнаруживаемые при низких скоростях нагрева (1 К/мин). Энергии активации α и γ переходов составляли, соответственно, 51.18 и 64.82 ккал/моль. Найдено, что температуры α и γ переходов прямо пропорциональны корню квадратному скорости нагрева.