

Determination of the Thermal Diffusivity of Calcium Salts of Saturated Carboxylic Acids¹

S. Stolik,² A. Valor,³ S. A. Tomás,^{4,5} E. Reguera,⁶ and F. Sánchez⁴

Calcium soaps are materials that serve a wide range of industrial applications such as softeners, detergents, plasticizers, greases, lubricants, cosmetics, and medicines. In addition, calcium salts of saturated carboxylic acids are of interest because of their presence in the staple food of Mexicans and other Central American people: the corn tortilla. Because of their wide use in industry, a knowledge of the thermal properties of the alkaline metal soaps is of great importance. In the present work, the thermal diffusivity of butyric-Ca, valeric-Ca, caprylic-Ca, undecanoic-Ca, palmitic-Ca, and stearic-Ca salts has been determined by photoacoustics. The thermal diffusivity of these salts shows a linear dependence on the number of carbons in the aliphatic chain, and was found within the range 2.60×10^{-3} to $1.38 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$, with the highest and lowest values corresponding to butyric-Ca and stearic-Ca, respectively.

KEY WORDS: calcium salts; carboxylic acids; open photoacoustic cell; thermal diffusivity.

1. INTRODUCTION

In the past few years, a number of studies have been devoted to clarify the mechanisms involved in the alkaline cooking (nixtamalization) of corn

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² Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear, 5ta. Ave. 502, Miramar, Playa, Ciudad de La Habana, Cuba.

³ Facultad de Física, Universidad de la Habana, San Lázaro y L, Vedado, Ciudad de La Habana, Cuba.

⁴ Departamento de Física, Centro de Investigación y de Estudios Avanzados-IPN, A.P. 14-740, México 07360 D.F., México.

⁵ To whom correspondence should be addressed. E-mail: stomas@fis.cinvestav.mx

⁶ Instituto de Materiales y Reactivos, Universidad de La Habana, San Lázaro y L, Vedado, Ciudad de La Habana, Cuba.

[1–3]. Nixtamalized corn products represent one of the most important ingredients in the basic diet of Mexicans and other Central American people. The formation of aliphatic calcium carboxylates during corn nixtamalization has been reported recently [4]. Special attention has been paid to these salts because of their wide use in the production of detergents, softeners, plasticizers, greases, lubricants, and cosmetics [5–8]. In addition, they play an important role in the areas of nutrition and medicine [9–12].

The synthesized calcium salts of carboxylic acids are monohydrates. From X-ray diffraction analyses, it has been concluded that these salts have monoclinic crystalline cells, described by the space group $P 21/a$, and contain four formula units ($Z = 4$) [13]. When the number of carbon atoms in the aliphatic chain increases, the cell parameter a grows linearly, while the cell parameters b and c remain almost constant, indicating that the structure is formed by stacked layers. The greater the number of carbon atoms in the aliphatic chain, the bigger the cell volume, which increases linearly.

Knowledge of the thermophysical properties of these salts is of importance for understanding the processes in which they participate. The lack of studies reporting the thermal characterization of such compounds should be noted. Usually, the physical and chemical properties, e.g., the thermophysical parameters, depend on the chain length, that is to say, on the number of carbon atoms in the chain [14, 15]. In the present work, the thermal diffusivity of calcium salts synthesized with 4, 5, 8, 11, 16, and 18 carbon atoms in the aliphatic chain, has been determined by the open photoacoustic cell (OPC) method.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Calcium salts were synthesized by mixing calcium hydroxide powder and liquid or solid acids. In the case of liquid acids, calcium hydroxide powder was mixed with an excess of liquid acids in an agate mortar. In the case of solid acids, these were added into a flask that contained distilled water at 85°C, and an aqueous solution of calcium hydroxide was subsequently added under vigorous agitation. In both cases, the obtained insoluble mixtures were washed in distilled water, filtered, and dried in air at room temperature. The obtained powders were washed repeatedly in chloroform and dried again at room temperature. The different analytical-grade reagents were obtained from Sigma (Sigma Chemical Company, St. Louis MO). The purity of the samples was checked by IR spectroscopy and X-ray powder diffraction.

A thermogravimetric analysis showed that the synthesized compounds were obtained as monohydrates, with the formula $(\text{CH}_3-(\text{CH}_2)_{N-2}-\text{CO}_2)_2 \text{Ca} \cdot \text{H}_2\text{O}$, where N indicates the number of carbon atoms in the chain. The density of the samples was determined with a density gradient column that contained different mixtures of *n*-hexane ($D = 0.663 \text{ g} \cdot \text{cm}^{-3}$) and CCl_4 ($D = 1.589 \text{ g} \cdot \text{cm}^{-3}$). These compounds were mixed at different volume ratios to obtain densities ranging between the two extreme values, with a resolution of $0.02 \text{ g} \cdot \text{cm}^{-3}$. The investigated samples included butyric-Ca, valeric-Ca, caprylic-Ca, undecanoic-Ca, palmitic-Ca, and stearic-Ca salts with N values given by 4, 5, 8, 11, 16, and 18, respectively.

The powders of calcium salts were pressed in a die (7T) to form discs of 200 to 300 μm thickness. For the photoacoustic (PA) measurements, an aluminum foil of 10 μm thickness was attached to one face of the samples in order to guarantee surface absorption of the incident light beam.

2.2. Photoacoustic Measurements

The thermal diffusivity can be accurately determined by photoacoustics. This technique looks directly at the heat generated in a sample, due to nonradiative de-excitation processes, following the absorption of light. The thermal diffusivity was measured with a home-made open photoacoustic cell arrangement [16]. The laser beam of a 180 mW Ar laser was modulated with a variable-speed mechanical chopper. The beam was directed to a sample mounted onto a cylindrical electret microphone. The front air chamber of the microphone was used as the typical gas chamber of conventional photoacoustics. The microphone signal provided the input to a lock-in amplifier (Stanford Research, Model SR850) interfaced to a PC. The photoacoustic amplitude and phase were displayed as a function of the modulation frequency of the incident light beam. Each sample was analyzed fivefold.

3. RESULTS AND DISCUSSION

The importance of the thermal diffusivity α as a physical parameter is that it is unique for each material, and reflects its strong dependence on the compositional and structural characteristics of the sample under analysis. The thermal diffusivity was determined from the thermal diffusion model for the PA effect, which states that for an optically opaque sample the pressure fluctuations are given by [17]

$$\delta p = \gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2} \exp(j(\omega t - \pi/2)) / \{2\pi T_0 l_g k_s f \sinh(l_s \sigma_s)\}, \quad (1)$$

where γ is the air specific heat ratio, P_0 is the ambient pressure, I_0 is the incident light beam intensity, T_0 is the room temperature, $f = w/(2\pi)$ is the chopping frequency, and l_i , k_i , and α_i are the thickness, thermal conductivity, and thermal diffusivity of material i , respectively. The subscript i denotes the sample (s) and gas (g) regions, and $\sigma_i = (1+j)a_i$, with $a_i = (\pi f/\alpha_i)^{1/2}$, is the complex thermal diffusion coefficient of material i . Particularly, for an optically opaque and thermally thick sample ($l_s\sigma_s \gg 1$), the expression for the photoacoustic amplitude S is given by

$$S = (A/f) \exp(-Bf^{1/2}), \quad (2)$$

where the constant A , apart from geometric constants, includes factors such as the light intensity, room temperature, and the gas thermal properties, and $B = (\pi l_s^2/\alpha_s)^{1/2}$. The thermal diffusivity α_s can thus be obtained from experimental data fitted with Eq. (2).

A typical dependence of the PA amplitude on the modulation frequency is presented in Fig. 1. It corresponds to a 270 μm thick undecanoic-Ca salt. The modulation frequency was scanned in the range 16 to

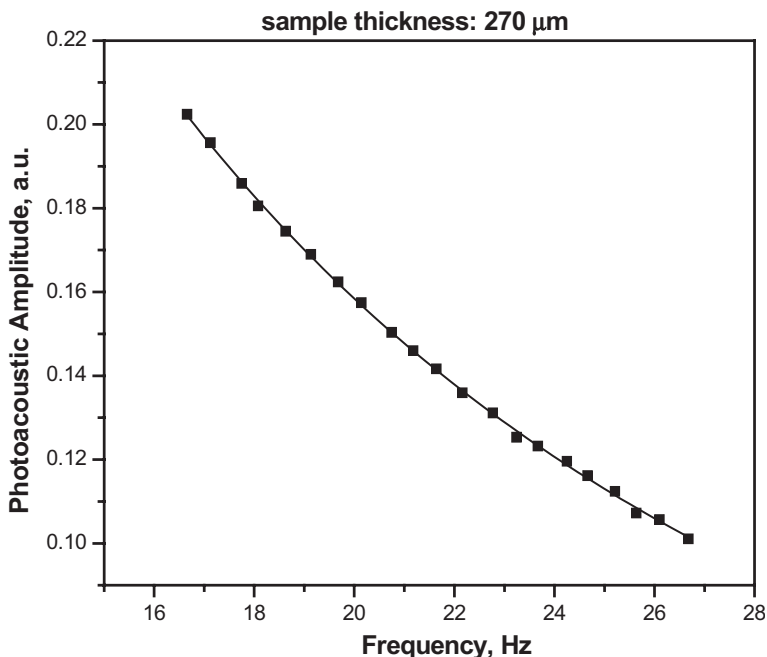


Fig. 1. Photoacoustic amplitude as a function of the modulation frequency of the incident light beam. It corresponds to an undecanoic-Ca salt. The solid line represents the best fit with Eq. (2).

Table I. Thermal Diffusivity (α) and Mass Density for Calcium Salts of Saturated Carboxylic Acids (The mass density was determined experimentally and calculated from X-ray diffraction patterns)

Sample	C_N	$\alpha \times 10^{-3} (\text{cm}^2 \cdot \text{s}^{-1})$	$D_m (\text{g} \cdot \text{cm}^{-3})^a$	$D_x (\text{g} \cdot \text{cm}^{-3})^a$
Butyric-Ca	C_4	2.6 ± 0.2	1.30	1.302
Valeric-Ca	C_5	2.7 ± 0.3	1.26	1.255
Caprylic-Ca	C_8	5.8 ± 0.6	1.18	1.152
Undecanoic-Ca	C_{11}	8.0 ± 0.5	1.09	1.102
Palmitic-Ca	C_{16}	10.6 ± 0.5	1.06	1.058
Stearic-Ca	C_{18}	13.8 ± 0.6	*	1.046

^a D_m : measured density; D_x : density calculated from XRD; * Not measured.

27 Hz. The thermal diffusivity for this sample was $8.0 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$. The thermal diffusivity for the investigated salts were found within the range 2.6×10^{-3} to $13.8 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$. The lowest value corresponded to butyric-Ca and the highest to stearic-Ca. The whole set of values are presented in Table I, along with the mass density. Two values are reported for the

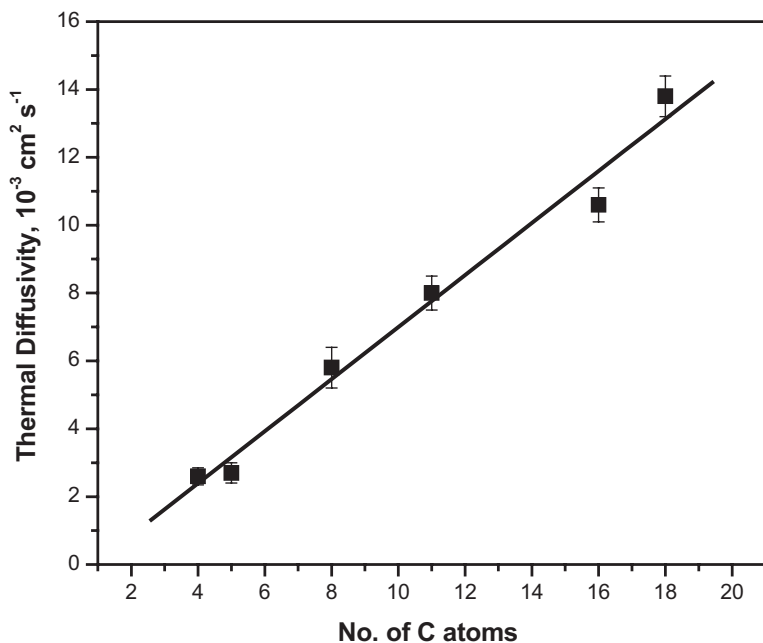


Fig. 2. Dependence of the thermal diffusivity on the number of carbons in the aliphatic chain of calcium salts of carboxylic acids.

mass density: the first value was measured with a density gradient column, whereas the second one was determined from X-ray diffraction patterns (not shown). Excellent agreement is observed between the measured and calculated values for the mass density. It has to be noticed that the mass density of the calcium salts decreases nonlinearly with an increase in the number of carbon atoms contained in the aliphatic chain.

As observed in Fig. 2, the thermal diffusivity shows an opposite effect, increasing linearly with the number of carbon atoms. In order to explain this result, we turn the attention to the expression for the thermal diffusivity $\alpha = k/(\rho c)$, where k is the thermal conductivity, ρ is the mass density, and c is the specific heat. As stated above, the mass density decreases with an increasing number of carbons. Moreover, there is a decrease in the relative mass of water M_{water} contained in these salts as the number of carbons increases in the chain. Here, M_{water} is defined as the ratio $M_{\text{H}_2\text{O}}/M_{\text{salt}}$, with $M_{\text{H}_2\text{O}}$ and M_{salt} denoting the molecular mass of water and a calcium salt, respectively. The inverse of M_{water} has been calculated and plotted in Fig. 3 as a function of the number of carbon atoms in the chain. Assuming that the specific heat of this type of carboxylic salts is mainly governed by the relative mass of water in the molecule, i.e., $c \propto M_{\text{water}}$, and consequently

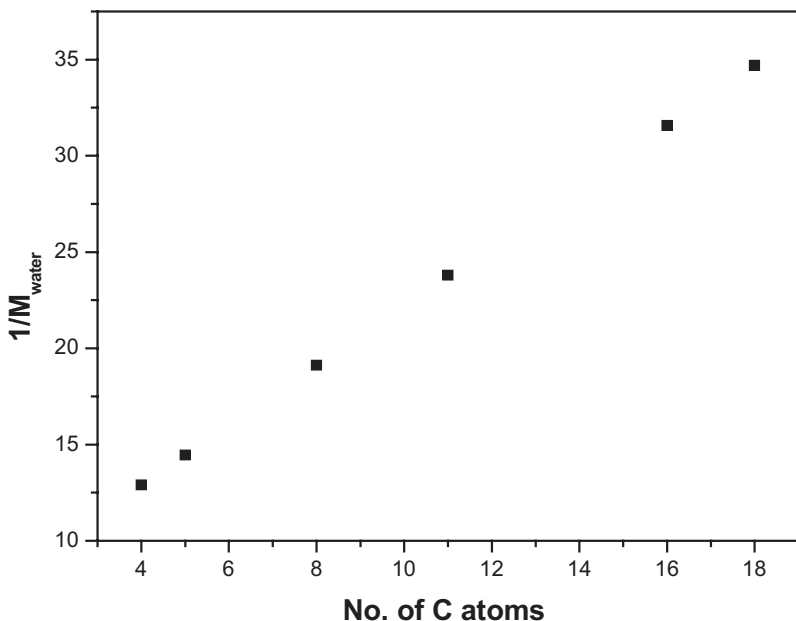


Fig. 3. Dependence of the inverse of the relative mass of water in calcium salts of carboxylic acids on the number of carbon atoms in the aliphatic chain.

$\alpha \propto 1/M_{\text{water}}$, the linear dependence of the thermal diffusivity on the number of carbon atoms may be chiefly attributed to the variations of the specific heat. As a consequence, the thermal conductivity is expected to be proportional to the mass density, decreasing nonlinearly with an increase in the number of carbon atoms contained in the aliphatic chain.

4. CONCLUSIONS

The thermal diffusivity shows a linear dependence on the number of carbons in the aliphatic chain of calcium salts of saturated carboxylic acids. Although the mass density decreases with a larger number of carbons, this effect is not sufficient to explain the thermal diffusivity behavior. Actually, it rather results from the loss of the relative mass of water in these salts, as the number of carbons increases in the chain. In order to fully understand the thermal behavior of the studied salts, further research on the specific heat and thermal conductivity of these compounds is needed.

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