DETERMINATION OF THE THERMAL DIFFUSIVITY OF CALCIUM SALTS OF SOME SATURATED CARBOXYLIC ACIDS

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ABSTRACT

Calcium soaps are materials that serve a wide range of industrial applications as softeners, detergents, plasticizers, greases, lubricants, cosmetics and medicines. Their selection for specific applications is governed by their fundamental properties. Calcium salts of saturated carboxylic acids are also of interest because of their presence in the staple food of Mexican and other Central American people: the corn tortilla. Because of their wide use in industry, the knowledge of the thermal properties of the alkaline metal soaps is of great importance. In the present work, the thermal diffusivity of a number of calcium salts of saturated carboxylic acids has been determined by photoacoustics. The obtained values were found within the interval 2.6×10^{-3} - 13.8×10^{-3} cm^2/s, corresponding to Butyric-Ca and Stearic-Ca, respectively.

Keywords: calcium salts, carboxylic acids, thermal diffusivity, open photoacoustic cell.

1. INTRODUCTION

In the last few years, a number of studies have been devoted to clarify the mechanisms involved in the alkaline cooking (nixtamalization) of corn. Nixtamalized corn products represent one of the most important ingredients in the basic diet of Mexicans and other Central American people [1-3]. 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.

The knowledge of the thermophysical properties of these salts is of importance for understanding the processes where they participate. It has to be noticed the lack of studies reporting the thermal characterization of such compounds. Usually, the physical and chemical properties, like the thermal ones, 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 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. An aqueous solution of calcium hydroxide was subsequently added; stirring was maintained during this preparation. 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 formula $(CH_3\text{-}(CH_2)_{N\text{-}2}\text{-}CO_2)_2Ca{:}H_2O$, 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 g/cm^3) and CCl_4 (D = 1.589 g/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 g/cm^3. The investigated samples include butyric-Ca, valeric-Ca, caprilic-Ca, undecanoic-Ca, palmitic-Ca, and stearic-Ca salts with N value given by 4, 5, 8, 11, 16, and 18, respectively.

The obtained powders were pressed in a die (7T) to conform discs of 200-300 μm thickness. For the photoacoustic (PA) measurements, an aluminum foil of 10 μm was attached to one face of the samples in order to guarantee superficial 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 non-radiative de-excitation processes, following the absorption of light. The thermal diffusivity was measured with a home-made open photoacoustic cell arrangement [17]. 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 light beam. Each sample was analyzed fivefold.

3. RESULTS AND DISCUSSION.

The importance of the thermal diffusivity α as a physical parameter to be monitored is because it is unique for each material, reflecting 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]

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

where γ is the air specific heat ratio, P_0 the ambient pressure, I_0 the incident light beam intensity, T_0 the room temperature, f 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 ($l_s \sigma_s >> 1$), the expression for the photoacoustic amplitude S is given by

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

where the constant *A*, apart from geometric constants, includes factors such as the light intensity, room temperature, and the gas thermal properties, and $a=(\pi\, l_s^2/\alpha_s)^{1/2}$. The thermal diffusivity α_s can thus be obtained from the experimental data fitting to expression (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 16-27 Hz. The thermal diffusivity for this sample was 8.0×10^{-3} cm^2/s. The thermal diffusivity for the investigated salts were found in the range 2.6×10^{-3} - 13.8×10^{-3} cm^2/s. The lowest value corresponded to Butyric-Ca and the highest to Stearic-Ca. The whole set of values are presented in Table 1, along with the mass density. Two values are reported for the mass density: the first was measured with a density gradient column, whereas the second one was determined from X-ray diffraction patterns (not shown). An 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 non linearly 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, growing linearly with the number of carbon atoms. In order to explain this result, we turn to the expression for the thermal diffusivity $\alpha=k/\rho c$, where *k* is the thermal conductivity, ρ the mass density, and *c* the specific heat. As stated above, the mass density decreases with a larger 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. 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 these type of carboxylic salts is mainly governed by the relative mass of water in the molecule, i.e. $c \propto M_{water}$, and consequently $\alpha \propto 1 / M_{water}$, the linear dependence of the thermal diffusivity may be chiefly attributed to the variations of the specific heat. Consequently, the thermal conductivity is expected to be proportional to the mass density. Nevertheless, in order to fully understand the thermal behavior of the studied carboxylic salts, new research on the thermal capacity *c* and thermal conductivity *k* of these compounds is needed.

CONCLUSIONS

The thermal diffusivity shows a linear dependence on the number of carbons in the aliphatic chain. 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. However, in order to fully understand the thermal behavior of the studied salts, new research on the specific heat and thermal conductivity of these compounds is needed.

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Table 1. 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	$\alpha \times 10^{-3}$ (cm^2/s)	D_m (g/cm^3)	D_x (g/cm^3)
Butyric-Ca	C_4	2.6 ± 0.25	1.30	1.302
Valeric-Ca	C_5	2.7 ± 0.3	1.26	1.255
Caprilic-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

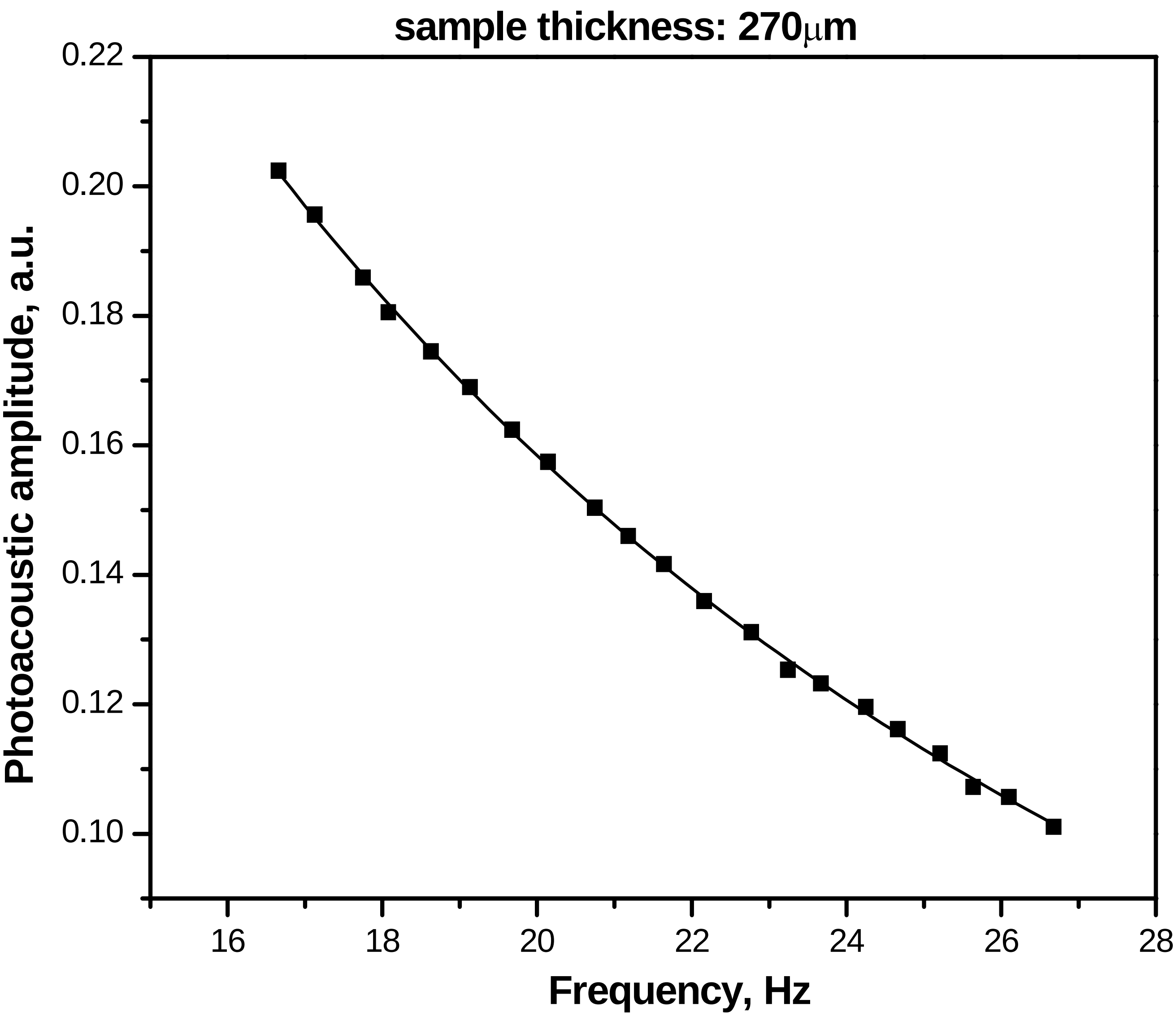
* Not measured. D_m- Measured density. D_x Calculated density from XRD

FIGURE CAPTIONS

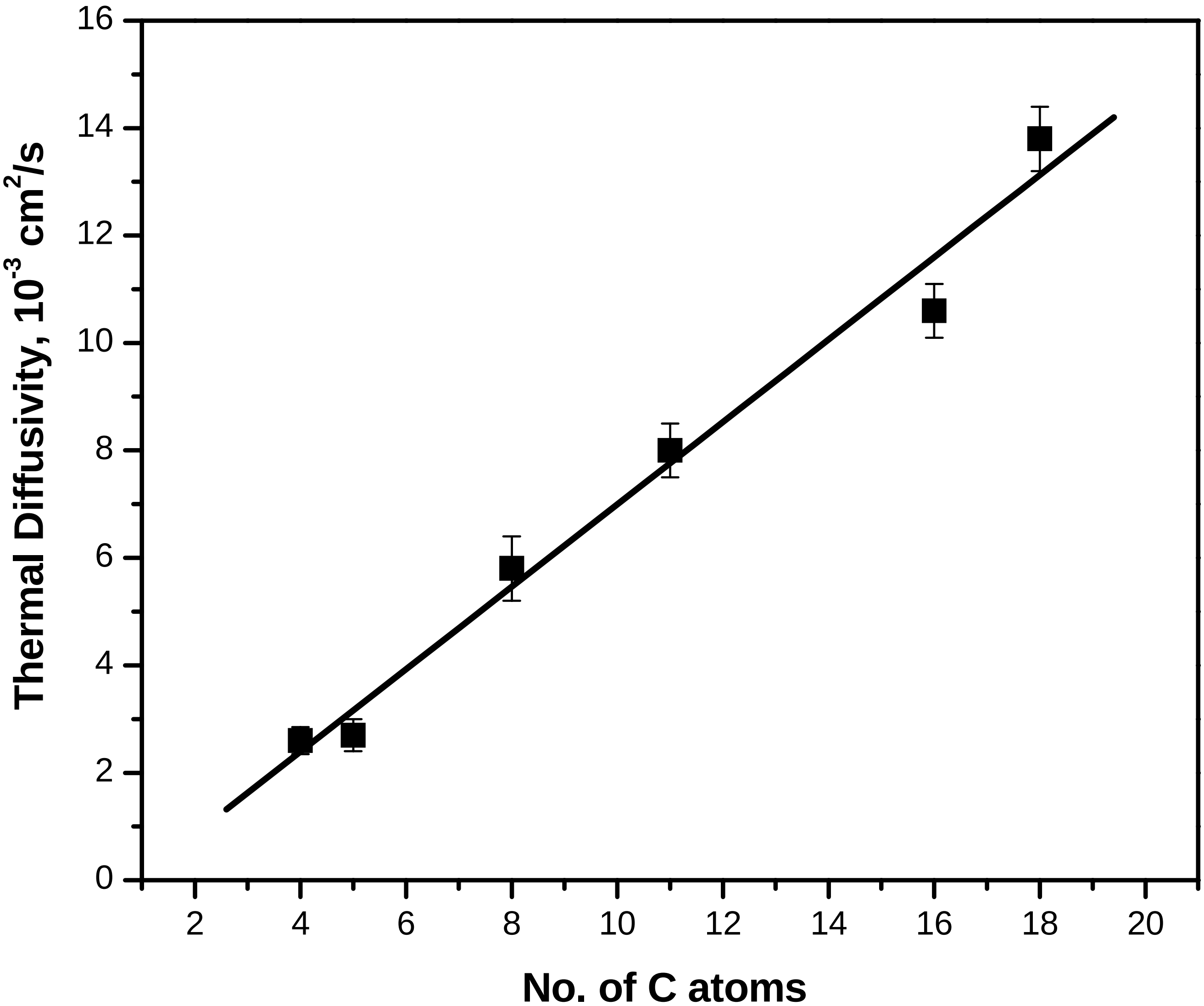
Fig. 1. Typical photoacoustic amplitude as a function of the modulation frequency of the light beam. It corresponds to an Undecanoic-Ca salt. The solid line represents the best fitting to equation (2).

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

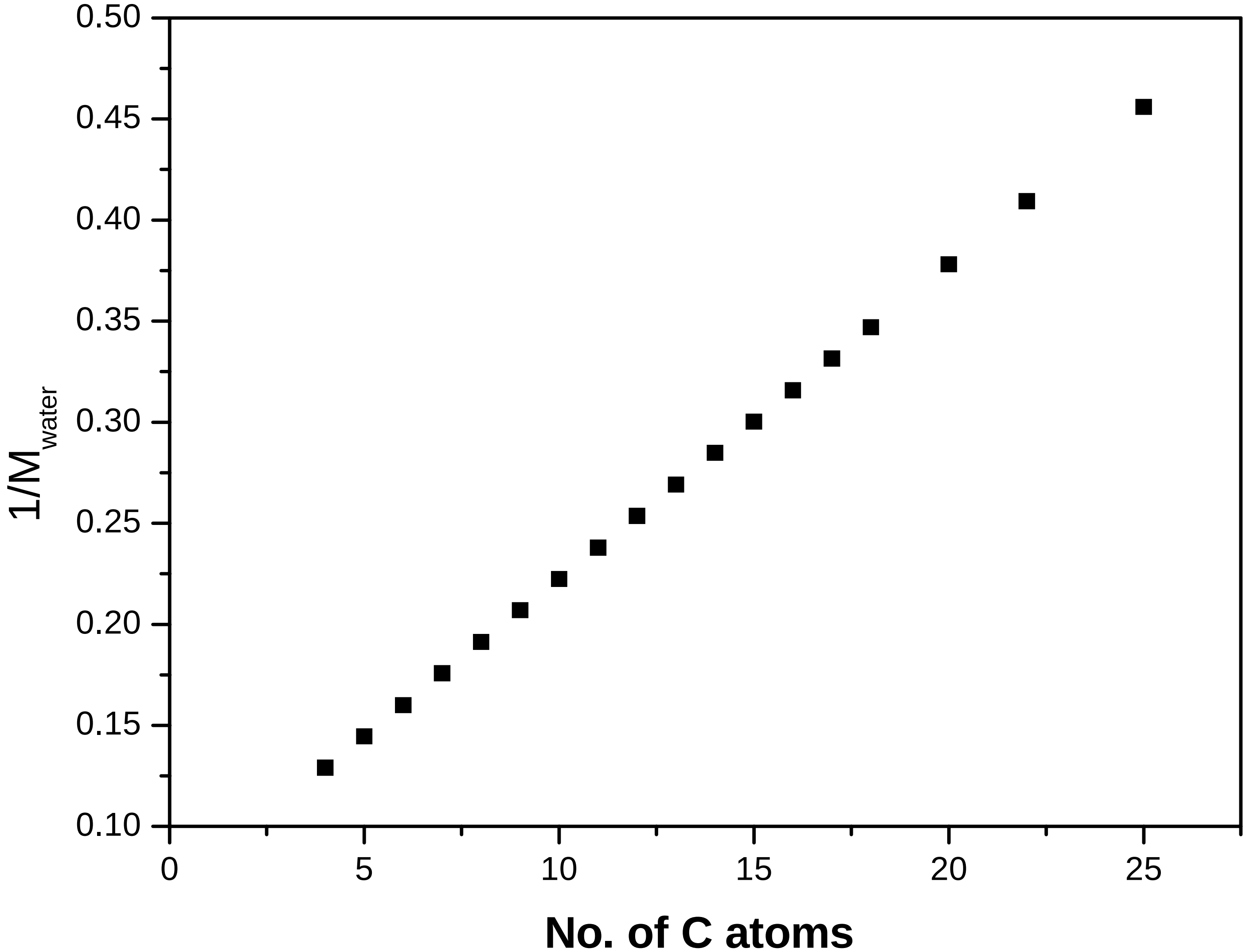
Fig. 3. Dependence of the inverse of the relative mass of water in calcium salts of carboxylic acids on the number of carbon atoms in the aliphatic chain.



sample thickness: 270μm
Photoacoustic amplitude, a.u.
Frequency, Hz
0.22
0.20
0.18
0.16
0.14
0.12
0.10
16
18
20
22
24
26
28



Thermal Diffusivity, 10-3 cm2/s
No. of C atoms
0
2
4
6
8
10
12
14
16
2
4
6
8
10
12
14
16
18
20



0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
$1/M_{water}$
0
5
10
15
20
25
No. of C atoms