Synthesis and X-ray diffraction study of calcium salts of some carboxylic acids[a)]

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An experimental X-ray diffraction (XRD) study of calcium salts of four carboxylic acids is presented. Calcium salts of propionic, butyric, valeric, and caproic acids were synthesized mixing in a mortar $Ca(OH)_2$ with the liquid acids. Measuring the thermogravimetric analysis curves it was determined that the salts were actually monohydrates. The densities of the synthesized samples were measured using a density gradient column. The measured values for the densities were as follows: $D_{m(\text{propionate})} = 1.38\ \text{g/cm}^3$, $D_{m(\text{butyrate})} = 1.30\ \text{g/cm}^3$, $D_{m(\text{valerate})} = 1.26\ \text{g/cm}^3$, $D_{m(\text{caproate})} = 1.22\ \text{g/cm}^3$. The XRD analysis revealed that these compounds have monoclinic cells with symmetry described by the $P2_1/a$ space group. Calcium propionate hydrate has cell parameters: $a = 2.437\,51(5)$ nm, $b = 0.681\,24(1)$ nm, $c = 0.591\,43(1)$ nm, $\beta = 95.320(2)°$. For calcium butyrate hydrate the cell parameters are: $a = 2.966\,84(8)$ nm, $b = 0.680\,74(2)$ nm, $c = 0.589\,29(2)$ nm, $\beta = 95.442(3)°$. The cell parameters for calcium valerate hydrate are: $a = 3.566\,36(4)$ nm, $b = 0.682\,49(1)$ nm, $c = 0.592\,77(1)$ nm, $\beta = 107.280(1)°$ and for calcium caproate hydrate $a = 4.180\,30(5)$ nm, $b = 0.682\,61(1)$ nm, $c = 0.592\,13(1)$ nm, $\beta = 110.230(1)°$. The calculated density values from the XRD results, taking into account that the number of chemical formulas in the unit cell equals four, agree very well with the measured ones. It was established that the unit cell parameter a grows with the increase of the number of carbon atoms in the aliphatic chain, while parameters b and c remain almost constant. This is an indication of the stacking layer character of the structure as has been suggested for calcium stearate monohydrate. This fact points to the possibility of the refinement of the crystalline structures taking as the starting point the reported structure for calcium stearate monohydrate. [DOI: 10.1154/1.1414011]

Key words: X-ray diffraction, carboxylic acids, calcium salts, TGA

I. INTRODUCTION

In Mexico the most consumed foods are corn products obtained through the lime treatment of corn grains with $Ca(OH)_2$. This way of cooking corn is known as *nixtamalization*. The obtained corn products have a high content of calcium, an important macroelement in human nutrition (Strewler and Rosenblat, 1995). Taking into consideration that these products are the fundamental source of Ca for the great majority of Mexicans it is important to know the ways Ca becomes available in order to manipulate and optimize the *nixtamalization* process. In a preliminary research on this topic, it was determined that one way of interaction of Ca with corn consists in the formation of Ca salts through the saponification of the fats present in the germ of the corn grain (stearic, palmitic, oleic, and linoleic acids) (Reguera *et al.*, 2000). As far as we know calcium salts of carboxylic acids have been poorly studied from the structural point of view. Only the structure of calcium stearate monohydrate has been solved (Lelann and Bérar, 1993). The pattern of the calcium propionate monohydrate has been previously reported (Charbonier *et al.*, 1977; PDF card 31-1585).

We have begun a systematic study of the calcium salts of carboxylic acids with several aliphatic chain lengths (from 3 to 30 carbon atoms in the chain) as part of a group of basic studies about the *nixtamalization* of corn and the properties of the corn products obtained in this way.

In the present work an X-ray diffraction (XRD) study of calcium propanoate monohydrate $[(C_2H_5CO_2)_2Ca{:}H_2O]$, calcium butanoate monohydrate $[(C_3H_7CO_2)_2Ca{:}H_2O]$, calcium pentanoate monohydrate $[(C_4H_9CO_2)_2Ca{:}H_2O]$, and calcium hexanoate monohydrate $[(C_5H_{11}CO_2)_2Ca{:}H_2O]$ is presented.

The diffraction patterns of the salts have been indexed, and the symmetry of the crystalline cells has been established.

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