# Fatty Acid Polymorph Identification by Infrared[1]

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## ABSTRACT

IR spectra in the 7.5-25.0 μm region are shown to be unique for polymorphic modifications of long chain saturated fatty acids of even carbon number and also for the individual fatty acids. IR spectra are presented for the A-, B-, C- and E-forms of stearic acid and for the C-form of myristic, palmitic, arachidic and behenic acid and the differences discussed. X-ray determined crystal long spacings for the A-, B-, C- and E-forms of a series of homologous even carbon-numbered acids are presented and compared with literature values. The formation of the different polymorphic forms are found to be temperature-concentration related and affected little by polarity of the solvent. Wideline nuclear magnetic resonance second moment values are given for the polymorphic forms of stearic acid.

## INTRODUCTION

In order to develop procedures and techniques for obtaining the various polymorphic forms of the long chain fatty acids, identification methods are first necessary. Wide line NMR analyses were recently shown applicable in differentiating between polymorphic forms of both saturated and unsaturated fatty acids (1). The method lacks specificity in identifying the individual acids and no information is obtained pertaining to crystal structure. X-ray diffraction patterns provide the crystal long and short spacing, which are in most instances a satisfactory means of identification for the various polymorphic forms of a given acid and also for the individual acids. The latter method lacks specificity, however, in that polymorphic forms of different acids can sometimes have very nearly the same crystal long spacing. Only when there is certainty of the identity of the acid can the individual polymorphs be identified, or conversely when the polymorphic form is known can the identity of the acid be established. IR as a means of identifying the long chain fatty acids and their various polymorphic modifications has not been exploited fully. Chapman (2) has used IR to study phase transitions of various polymorphic modifications of acids of both odd and even numbers of carbon atoms, but limited his study to the 2.5-15.0 μm region. Bentley et al. (3) have explored the 700-350 $cm^{-1}$ region of the spectrum and were able to distinguish between monocarboxylic acids in a series ranging from formic to stearic acid. The authors, although having taken care to insure that the acids were in the most stable form by crystallizing them from the melt, did not attempt further to identify the specific polymorphic form. In a recent publication, Holland and Nielsen (4) reported the existence of a fourth polymorphic form of the even carbon-numbered saturated acids, the E-form. Their identification was based on differences in the IR spectra of the individual forms by determination with polarized light.

In the present report, IR in the 7.5-25.0 μm region is presented as a method for identifying the individual even carbon-numbered fatty acids and specific polymorphic modifications. Identification by IR is compared with X-ray

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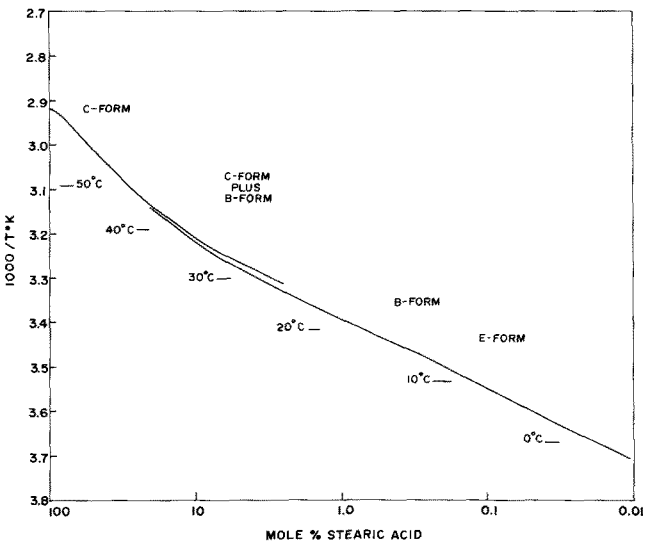


FIG. 1. Solubility curve for stearic acid in toluene illustrating areas of different polymorph formation.

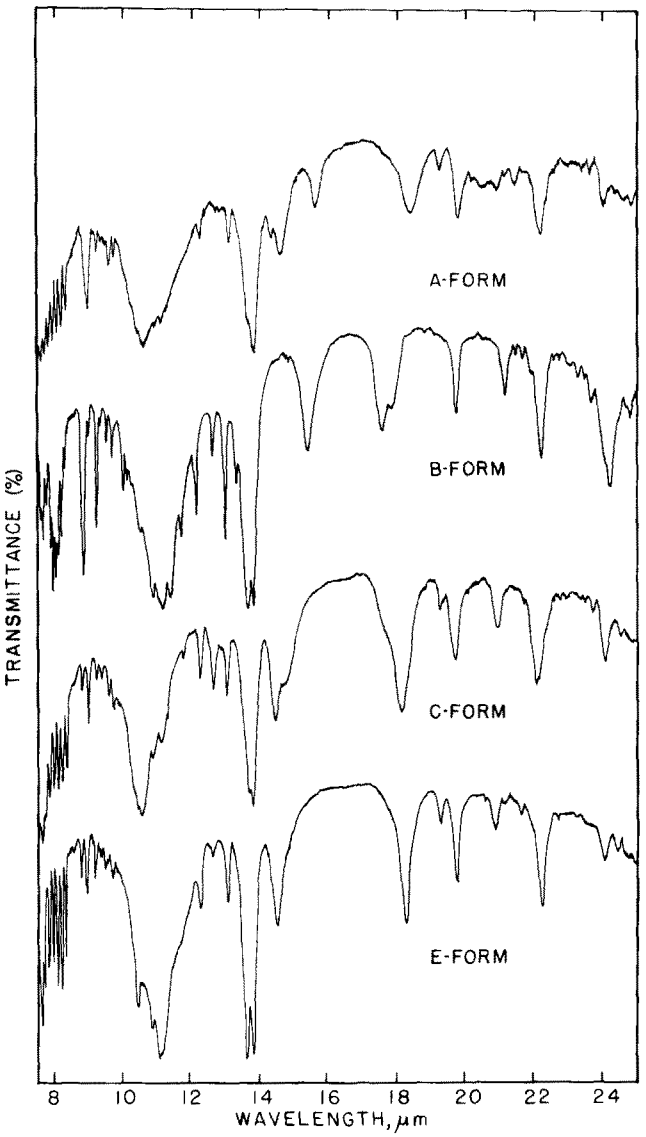


FIG. 2. IR spectra for the A-, B-, C- and E-forms of stearic acid.

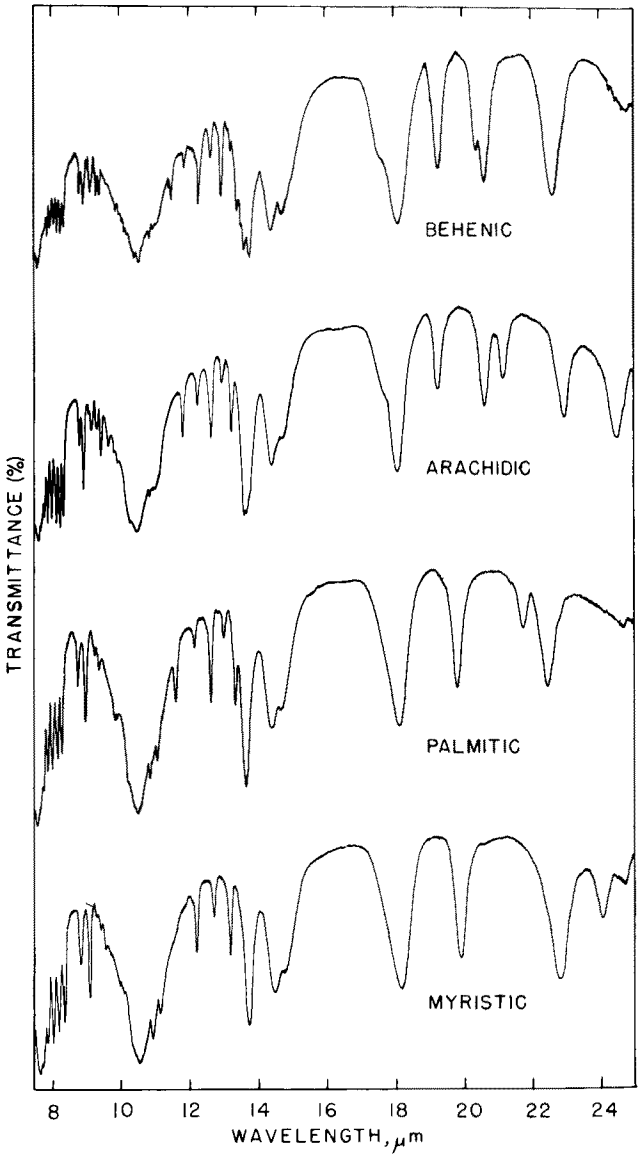


FIG. 3. IR spectra for the C-form of myristic, palmitic, arachidic and behenic acids.

and wide line NMR determinations. Conditions are described for the formation of various polymorphic modifications.

## EXPERIMENTAL PROCEDURES

The fatty acids used in this investigation were recrystallized materials from fractionally distilled methyl esters. The recrystallized fatty acids had freezing points which compared well with literature values. The stable C-forms of the acids were obtained by recrystallization from the melt at room temperature (ca. 23 C). The various metastable polymorphic forms of the different acids were obtained by solvent crystallization at temperatures and concentrations to be discussed. The solvents used were all reagent grade.

A conventional spectrophotometer, the Perkin-Elmer model 337, was used. The spectrophotometer was operated at ambient temperature under the following conditions: slit program normal and scan slow (24 min). The spectrophotometer was adjusted with air against air.

The spectra were obtained using either thin films crystallized between KBr plates or "Nujol" mulls between KBr plates.

A General Electric diffractometer model XRD-5 was used to obtain the X-ray diffractions by the direct recording on a strip chart. The instrument was equipped

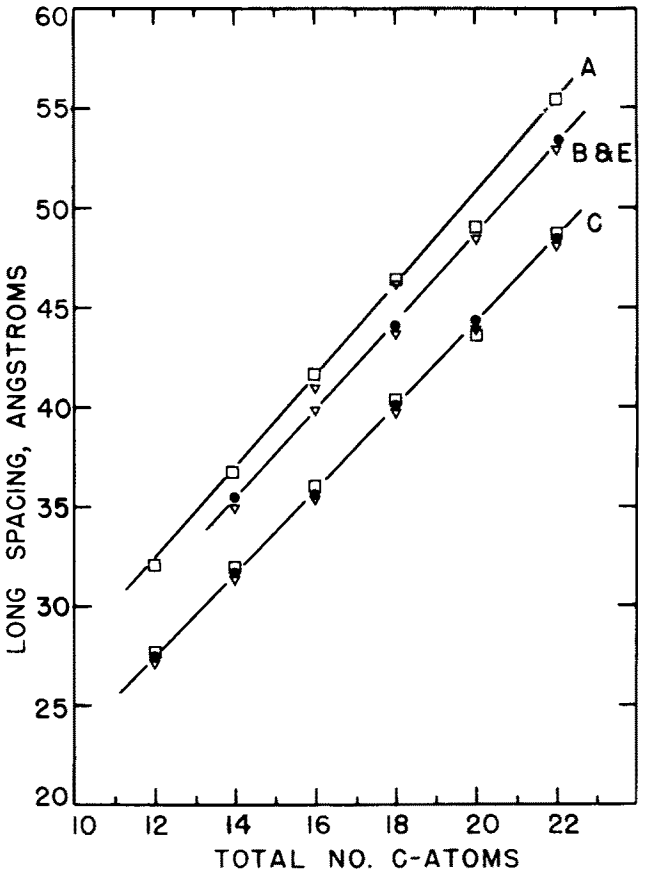


FIG. 4. Crystal long spacing–total number of C-atoms relationship for A-, B-, C- and E-forms of even carbon-numbered fatty acids. Closed circles, our data; open triangles, Francis et al. (6); open squares, Stenhagen and von Sydow (7).

with a copper target X-ray tube, and a 0.0007 in. thick nickel filter. A 1° slit was used in collimating the 20° angle between 0° and 50°. The X-rays were generated at 45 KVP and 15 ma. The diffraction patterns were determined on smooth-faced pressed samples, ca. 1 mm thick.

Wide line NMR spectra were obtained with a Varian VF 16F spectrometer at ambient temperature. Pertinent instrument parameters were: RF frequency 16 MHz; sweep width, 50 gauss; sweep rate, 2 gauss/min; modulation sweep width, 2.6 gauss.

## RESULTS AND DISCUSSION

The formation of the various polymorphic forms of long chain fatty acids is influenced by a number of factors: purity, carbon chain length, whether the carbon chain contains an odd or even number of carbon atoms, solvent crystallization temperature, and solubility of the acid in the particular solvent. Polarity of the solvent was not found to be a factor other than as it affected the solubility of the acid. Generally the long chain, even carbon-numbered fatty acids (12-22 C-atoms), when allowed to crystallize from the melt at room temperature (ca. 23 C), do so in the stable C-form. Solvent crystallization, on the other hand, can give any of the four forms either single or as mixtures of different forms. Behenic and stearic acids were crystallized at a number of different temperatures from benzene, toluene, *n*-hexane, petroleum ether, acetone, methanol and ethanol. Although an in-depth investigation of the precise conditions for the formation of the different polymorphic forms was not carried out for each of the solvents mentioned, the molar concentration of the acid was observed to be the primary factor determining which polymorph was obtained from most solvents. A typical solubility curve is shown in Figure 1 to illustrate the

temperature-concentration areas in which the B-, C- and E-forms of stearic acid are obtained from toluene. It should be noted that between 20-50 C both the B- and C-forms are crystallized from solution. The conditions for determining the two solubility curves have been discussed previously (5). The B- and E-forms of the acids were obtained in each instance by evaporation of the toluene at reduced pressure between 20-10 C and 10-0 C, respectively. The C-form was obtained exclusively when the crystals were allowed to form above 50 C. Pure A-form was prepared by allowing the crystals to develop slowly over a several month period in a saturated solution with toluene at normal room temperature. The A-form is recognized easily by the long needle-like crystals as compared to the plates of the B-, C- and E-forms.

IR spectra for the 7.5-25.0 $\mu$m region were obtained for the various polymorphic forms of homologous saturated acids. The series included those acids from lauric to behenic. Absorption bands characteristic of the individual polymorphs were noted, although all four polymorphs of each acid were not obtained. Typical spectra of the four polymorphic modifications of stearic acid are illustrated in Figure 2. The spectra of the four forms differ as a result of their crystal structure in three general regions: 10.0-11.5, 14.5-15.5 and 17.0-18.5 $\mu$m.

The spectra were also observed to be distinctive for each of the acids in the series. These differences occurred between 19.0-25.0 $\mu$m, as illustrated in Figure 3 by the spectra of the C-form of myristic, palmitic, arachidic and behenic acid. Similar differences were observed in comparisons of the A-, B- and E-forms of the acids.

X-ray diffraction data were obtained on the different forms of the acids. Surprisingly the B- and E-forms had very nearly identical crystal long spacings with no significant differences in patterns or intensities. Single crystal measurements for the B- and E-forms of stearic acid have revealed unit-cell and $\beta$-angle differences which will be discussed in a later publication. Stearic acid was the only acid of which the pure A-form was obtained. The A-forms of the other acids obtained contained varying amounts of the other polymorphic modifications.

In Figure 4 is illustrated the relationship between crystal long spacing and total number of carbon atoms. The identical long spacings for the B- and E-forms are shown. Crystal long spacings from the literature (6,7) are also included for the A-, B- and C-forms for comparison.

NMR spectra were obtained for the A-, B- and C-forms of stearic acid. Spectra for the E-form of stearic and behenic acids were of poor quality and were not suitable for calculation of line width or second moment. The poor quality spectra can be explained possibly on the basis of saturation effects caused by very long spin lattice relaxation times. Second moment values for the A-, B- and C-forms were 21.7, 43.3 and 19.6 gauss$^2$, respectively. High second moment values are indicative of high proton mobility and rigid lattice structures.

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