

THE DIFFRACTION OF X-RAYS IN LIQUID NORMAL
MONOBASIC FATTY ACIDS

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ABSTRACT

Eleven of the normal monobasic fatty acids in the liquid state have been investigated with $\text{MoK}\alpha$ radiation. The results are similar to those previously reported for the liquid primary normal alcohols by Stewart and Morrow. There are two spacings found by the application of Braggs' law, one of which is the lateral separation of the molecules which lie in parallel collinear chains and the other the separation of the planes passing transversely through the chains and containing the diffraction centers of the molecules. The lateral spacing is 4.55A for the samples having more than five carbon atoms to the molecule. This is in agreement with the values found by Stewart and Morrow for the primary n-alcohols and with the work of Adam on monomolecular films. The longitudinal spacing varies linearly with the carbon content, the increase being 2.00A for two molecules. In the molecular arrangement, the chains are not normal to the transverse planes and there are two molecules in series, with associated COOH groups, for each spacing. A comparison of data for the acids in the liquid and crystalline states shows that the arrangement of molecules in the cybotactic state is not that found in the crystalline state.

INTRODUCTION

THE present work is a continuation of an investigation of the x-ray diffraction in liquid primary normal alcohols.¹ The fatty acids investigated are long chain compounds terminated at one end by a CH_3 group and at the other end by a COOH group. The object of this study is to secure more evidence of a distinct space array in liquids, called the cybotactic state, and to make a comparison of spacings found for the substances in the crystalline and liquid states.

The apparatus and experimental procedure are essentially the same as previously described.¹ The ionization chamber method and $\text{MoK}\alpha$ radiation are used. The liquid normal fatty acids from formic (CH_2O_2) to undecylic ($\text{C}_{11}\text{H}_{22}\text{O}_2$) are investigated. Propionic, butyric, valeric, caproic, heptoic, caprylic, pelargonic, capric and undecylic acids were obtained from the Eastman Kodak Company. Formic, acetic, butyric, valeric, and heptoic acids were obtained from the American Krueger and Toll Company.

EXPERIMENTAL RESULTS

The results for the liquid normal monobasic fatty acids are shown in the form of graphs in Fig. 1. Each curve is the mean of three or more sets of observations. For the purpose of comparison of curves it has been found convenient to multiply the diffraction intensity in each case by a factor so that the principal maximum is of the same height. The curves are designated

¹ Stewart and Morrow, Phys. Rev. 30, p. 232 (1927).

by the number of carbon atoms in the molecule, and are separated in the graph by a displacement of the ordinates.

The curves shown in Fig. 2 are for liquid and solid capric acid. The melting point of capric acid is 31°C . The curves for the solid were made at room temperature. The curves for the liquid were made just above the

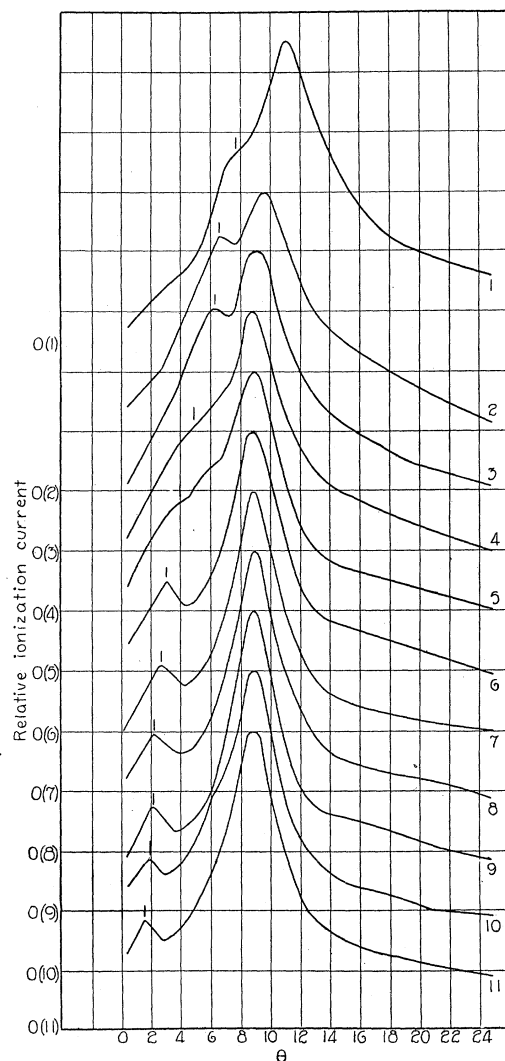


Fig.1. Intensity-diffraction curves with fatty acids containing from one to eleven carbon atoms.

melting point. The chief computed spacings for the crystal, 23.4A, 4.2A and 3.7A, are in agreement with the results of Trillat,² 23.3A, 4.4A and 3.6A, and with those of Gibbs,³ 23.3A, 4.2A, 3.7A and 3.4A.

² Trillat, *Ann. d. Physique* **6**, p. 5 (1926).

³ Gibbs, *Journal Chem. Soc. London* **125**, p. 2622 (1924).

DISCUSSION OF RESULTS

From the experimental curves for the liquid acids, Fig. 1, it is evident that there are two peaks in the ionization intensity curve. Fig. 3 shows the

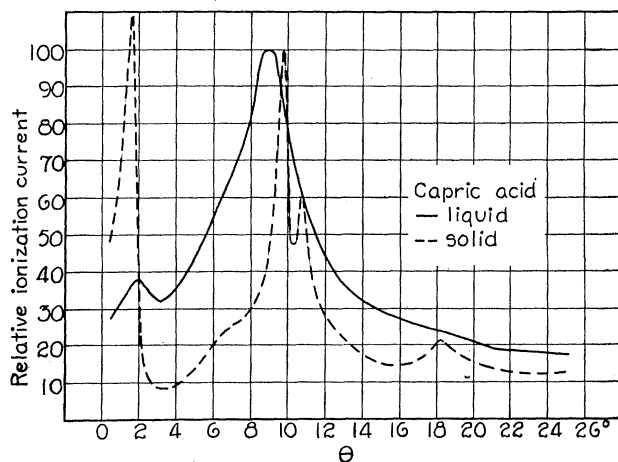


Fig. 2. Diffraction curves for solid and liquid capric acid.

values of the corresponding "planar" spacings, computed by Bragg's law, plotted against the number of carbon atoms in the molecule. The observed points indicated by the circles are those of the author, those by crosses were

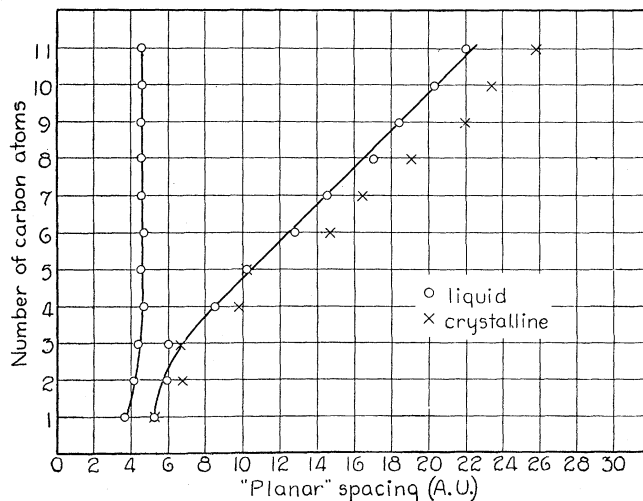


Fig. 3. Variation of "planar" spacing with carbon content of the molecule.

obtained by Gibbs.³ One of the spacings indicated by the curve in Fig. 3 varies linearly with the carbon content of the chain for the higher members of the series, and hence is associated with the length of the molecule. The

other spacing does not vary appreciably under these circumstances and is therefore normal to the chains and is the *diameter* of the chain. It follows that the molecular chains are aligned parallel. Since the acid molecule is polar, the carboxyl group forming the active end, it is to be expected that the two active ends of neighboring molecules in these rows will be together. These two carboxyl groups provide the necessary excess of diffracting material along the double length of molecules to account for the peak which varies with the length of the chain. Thus the effective planes containing the carboxyl groups are separated by the length of two molecules. This conclusion is further verified by the quantitative discussion below. It is the one reached by Müller,⁴ Müller and Shearer⁵ and Trillat² for the crystalline long chain compounds.

According to the above arrangement the angle that the direction of the chain makes with the normal to the planes of long spacing is the only unknown factor. If the density is computed roughly by the use of the formula

$$\rho = \frac{2(\text{mol. wt})(\text{mass of } H. \text{ atom}) \cos \gamma}{d_1 d_2^2}$$

where d_1 is the long spacing, d_2 is the spacing due to the diameter of the molecule, and γ is the angle the length of the molecule makes with the normal to the planes of long spacing and is arbitrarily made 50° , the resulting values are as shown in Table I. Since the *diameter* here found is a mean value, and for other obvious reasons, the computation just given should not be accepted as definitely determining the molecular arrangement.

TABLE I
Values of the spacing constants d_1 and d_2 .

Acid	Number of carbon atoms	Molecular weight	Actual density	d_2	d_1	ρ
Formic	1	46.01	1.22*	3.65	5.2	1.42
Acetic	2	60.06	1.05*	4.17	5.9	1.25
Propionic	3	74.05	.992*	4.39	6.0	1.36
Butyric	4	88.06	.959*	4.64	8.5	1.03
Valeric	5	102.08	.942*	4.54	10.2	1.03
Caproic	6	116.09	.929*	4.64	12.8	.90
Heptolic	7	130.11	.922*	4.54	14.5	.93
Caprylic	8	144.12	.910*	4.54	17.0	.88
Pelargonic	9	158.14	.907*	4.54	18.4	.89
Capric	10	172.15	.859 ⁺	4.59	20.3	.86
Undecylic	11	186.17	—	4.54	22.0	.88

* At 20°C . ⁺At 30°C . From International Critical Tables.

The agreement between computed and actual densities is good for the higher members of the series; in fact there is a maximum difference of only 4 percent if the first three in the series are omitted.

There is another computation of importance. The slope of the curve in Fig. 3 shows that the increase in spacing for each pair of CH_2 groups (two

⁴ Müller, Journal Chem. Soc. London **123**, p. 2043 (1923).

⁵ Müller and Shearer, Journal Chem. Soc. London **123**, p. 3156 (1923).

molecules) is 2.0A. This is precisely the value found by Müller⁴ and compares favorably with that of Trillat,² 2.14A, for the much longer solid fatty acid chains with an even number of carbon atoms. Gibbs³ results, shown in Fig. 3, give a value 2.45A corresponding with Trillat's results for the odd number of carbon atoms.

But a difficulty arises in the fact that if the angle of inclination of the molecules to the normal to the planes is assumed to be 50°, the length of the chain occupied by one carbon atom is $1.0/\cos 50^\circ$ or 1.56A. This would probably mean, since the distance of separation in diamond is 1.54A, that the carbon atoms are arranged in line and not zigzagged as has been the case with the solid fatty acids in the contributions herein cited. It seems easier to doubt the assumed 50° and the precise arrangement given than the non-linear arrangement of carbon atoms.

As is shown in Fig. 3, in every case the long spacing for the crystal is larger (about 15 percent) than that found for the same material in the liquid state in this work. For most of the acids Gibbs³ also reports other "broad line" spacings having values from 3.5A to 4.3A. In every case for which these spacings are reported for the crystalline material the values given are smaller than the one spacing found in this region for the liquid.

Since in passing from the crystalline to the liquid state there is an increase in the distances associated with the cross section of the molecule and a decrease in the other spacings, it is evident that the molecules are rearranged. The structure in the cybotactic state is thus, as presumed, not identical with that of the same material below the melting point.

In the crystalline state the peaks are very sharp. The principle factor in determining the peak width is the size of the slits of the spectrometer. In the case of liquids, however, the peaks are very broad. It is to be expected that in passing from the crystalline to the cybotactic state the peaks will become broader due to the variation of spacings present in the cybotactic state. There is also the possibility that the broad peak in liquids is due to two sets of spacings of very nearly the same value.

Attention should be called to the agreement with the *diameter* of the fatty acid molecules found in the monomolecular layers on liquid by Langmuir⁶ and Adam.⁷ Their value of the cross sectional area for the case of the film on water is 21×10^{-16} cm⁻² or almost exactly the square of our *diameter*, about 4.57A. Also, it is the same diameter as that found⁸ for the liquid primary n-alcohols and for the liquid paraffins.⁹

Sogani¹⁰ has taken diffraction photographs of some of the liquid acids herein discussed. They are formic, acetic, butyric and lauric. Except in the case of acetic acid he did not find the second peak which is highly important. This is doubtless because of the resolving power of his instrument.

⁶ Langmuir, Jour. Am. Chem. Soc. **39**, p. 1848 (1917).

⁷ Adam, Proc. Roy. Soc. **A101** p. 452 (1923) and **103**, p. 723 (1923).

⁸ Stewart and Morrow, Phys. Rev. **30**, p. 232 (1927).

⁹ Stewart, Phys. Rev. **31**, 000 (1928).

¹⁰ Sogani, The Indian Journal of Physics, vol. 2, part 1, 1927.

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