An entirely new modification of fatty acids was discovered in the case of the C_{14} acid.

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x-Ray Studies of Mixtures of Fatty Acids[1,2]

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Introduction

x-Ray studies on well-defined mixtures of long chain compounds are relatively few. Most of the results available so far we owe to Piper and his co-workers.[3]

Since we had a series of unusually pure fatty acids available and since we are particularly interested in mixtures of long chain compounds from the standpoint of polymerization, this study was undertaken.

Experimental

I. Two-Component Mixtures of Fatty Acids

1. **General.** (a) **Preparation of Samples.**—All samples of the mixtures were prepared by the same method. In each case, samples of the acids were weighed out to 0.0001 g. The acids were then fused together in a watch glass and kept just above the melting point for some time. Continual stirring with a small glass rod assured thorough mixing of the several components. The entire mass was then solidified by rapid cooling.

The sample plates were prepared by melting and subsequent solidification of portions of these mixed samples on glass plates. Whenever a check was run on any sample, a second portion of the mixture was taken solidified on a glass plate, and then remounted in the spectrograph. The materials used and the x-ray technique are the same as used in the previous investigation.[4]

(b) **Explanation of Tables.**—Whenever the deviation for a value is listed, it will be the maximum deviation from the mean in Ångström units. Where more than one value is listed for a particular mixture, it is a check on the reproducibility of the result, unless otherwise explained. The final

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[1] From a thesis submitted by F. B. Slagle in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

[3] Hydrocarbons: S. H. Piper, D. Brown and S. Dyment, *J. Chem. Soc.*, **127**, 2194 (1925); G. L. Clark, *Nature*, **120**, 12 (1927); S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931). Acids: S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926); also F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A126**, 214 (1930).

[4] F. B. Slagle and Emil Ott, THIS JOURNAL, **55**, 4396 (1933).

column in the graphs represents the best value or values for the spacings of the (001) plane of the mixtures. The composition of all of the mixtures is given in mole percentages.

2. Systems with Components which Are One Carbon Atom Apart.—Mixtures of capric (C_{10}) and undecylic (C_{11}) acids were studied in ten equal steps. In Table I are listed the spacings obtained from these mixtures, and in graph I their plot is given. Figure 1 shows prints of three of the C_{10}–C_{11} mixtures together with pure C_{10} and pure C_{11}. It is observed that the lines obtained from the mixtures are comparable in sharpness with those obtained from the pure acids, and that each mixture gives a single spacing.

TABLE I

C_{10}–C_{11} MIXTURES

Mole % C_{10}	Mole % C_{11}	Spacing with dev.		Av. spacing
0.0	100.0	25.32		25.32
10.7	89.3	25.03 ± 0.04		25.03
20.8	79.2	24.69 ± 0.03		24.69
30.2	69.8	24.55 ± 0.02		24.55
41.8	58.2	24.37 ± 0.04	24.39 ± 0.05	24.38
51.8	48.2	24.20 ± 0.01	24.20 ± 0.01	24.20
61.9	38.1	23.71 ± 0.01		23.71
71.4	28.6	23.58 ± 0.01		23.58
81.2	18.8	23.33 ± 0.00		23.33
90.7	9.3	23.19 ± 0.02		23.19
100.0	0.0	23.02		23.02

Typical results on these C_{10}–C_{11} mixtures are as follows: mole % C_{10} = 51.8; mole % C_{11} = 48.2; $\sin \Theta/n$ = 0.03179 (com.), 0.03179, 0.03178 (com.) and 0.03182 (wk); average = 0.03179; d = 24.20 Å.

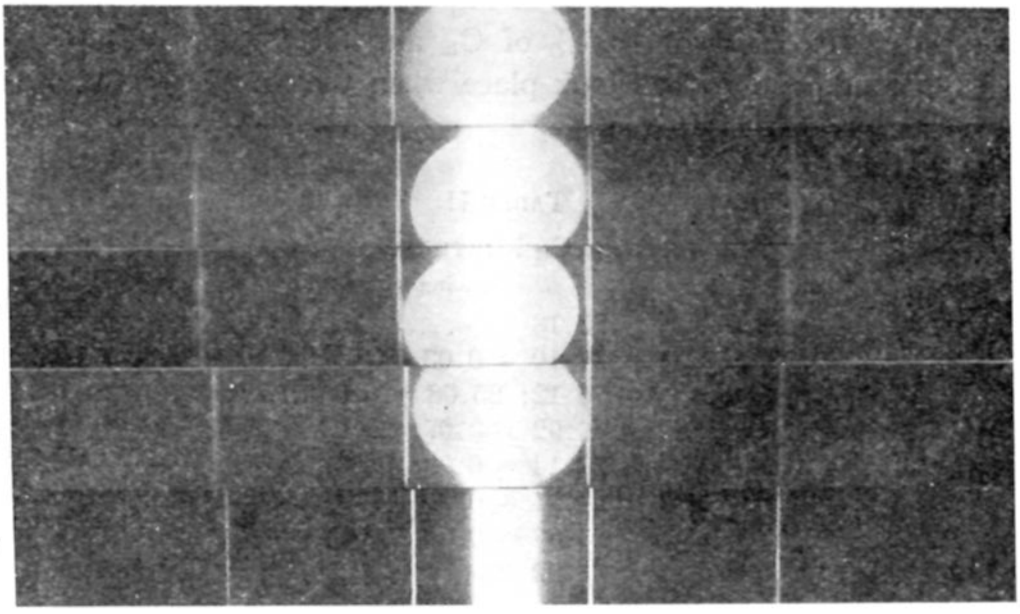

Fig. 1.—C_{10}–C_{11} acid mixtures: a, pure C_{10} acid; b, C_{10} = 81.2%; C_{11} = 18.8%; c, C_{10} = 61.9%; C_{11} = 38.1%; d, C_{10} = 30.2%; C_{11} = 69.8%; e, pure C_{11} acid.

3. Systems with Components which Are Two Carbon Atoms Apart. **(a) C_{10}–H_{12} Acid Mixtures.**—Table II gives the spacings obtained for the various mixtures of C_{10} and C_{12} fatty acids which were studied. It is observed that in the case of two of the mixtures more than one spacing is reported. That these spacings correspond to different modifications for these particular mixtures, and not to phases of different composition, was proved for the mixture of 43.8% of C_{10} and 56.2% of C_{12} as follows. The sample was prepared in the usual manner and a picture taken immediately. Two spacings were observable which were 25.12 Å. and 25.90 Å. The same sample plate was exposed two days later and gave two spacings: 25.08 Å. and 26.92 Å. After a total of two weeks, this sample plate was again exposed and this time just one spacing of 26.92 Å. was observed. Thus the spacing of 25.90 Å. observed on the first picture corresponds to a rather unstable modification which changes over completely to a second modification having a spacing of 26.92 Å. During this change the amount of the remaining modification corresponding to 25.10 Å. (average of 25.12 and 25.08) was practically unchanged, judging from the intensities of the lines. However, upon standing for two weeks it also changed to the modification with the spacing of 26.92 Å.

This same explanation holds for the mixture of C_{10} = 53.4% and C_{12} = 46.6%. Here, however, only two spacings are observed; the modification having the spacing of 26.14 Å. is present in small amounts, and upon standing changes over into a more stable modification which has the spacing of 25.31 Å.

Plots of the spacings obtained for the C_{10}–C_{12} mixtures are given in graph II. Prints of pure C_{10} and of pure C_{12} together with several of the mixtures are given in Fig. 2. Also in Fig. 2 are given prints of the mixture having the composition of 43.8% of C_{10} and 56.2% of C_{12} showing the changes in modification that took place when the sample was allowed to stand over a period of two weeks.

TABLE II

C_{10}–C_{12} MIXTURES

Mole % C_{10}	Mole % C_{12}	Spacing with dev.	Av. spacing
0.0	100.0	27.18	27.18
22.5	77.5	27.10 ± 0.03	27.10
43.8	56.2	25.12; 25.08 ± 0.03; 25.90 26.92 ± 0.07; 26.92 ± 0.04	25.10 25.90 26.92
53.4	46.6	26.14 ± 0.02; 25.31 ± 0.02	26.14 25.31
63.2	36.8	24.94 ± 0.03	24.94
82.6	17.4	23.53 ± 0.05; 23.54 ± 0.04	23.54
100.0	0.0	23.02	23.02

A typical calculation on these C_{10}–C_{12} mixtures is as follows: mole % C_{10} = 22.5; mole % C_{12} = 77.5; $\sin \Theta/n$ = 0.02839 (com.), 0.02839, 0.02836 (com.) and 0.02842; average = 0.02839; d = 27.10 Å.

(b) C_{16}–H_{18} Acid Mixtures.—This work on mixtures of palmitic (C_{16}) and stearic (C_{18}) acids is a repetition of the work reported by Piper, Malkin and Austin[5] on these same two acids, except that the mixtures have slightly different compositions. Each mixture gave a single spacing, the lines for these mixtures being as sharp as those for the pure acids. Table III gives the spacings for the mixtures of C_{16} and C_{18} acids, and graph III gives the plot of these spacings.

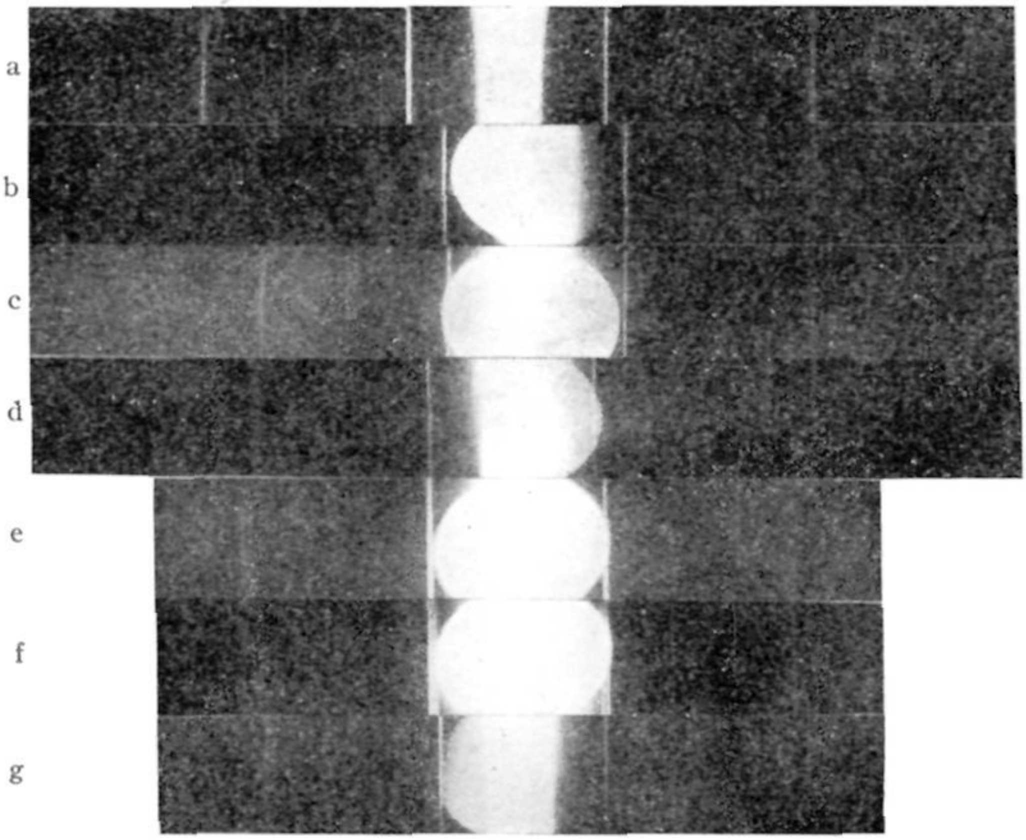

Fig. 2.—C_{10}–C_{12} acid mixtures: a, pure C_{10} acid; b, C_{10} = 63.2%; C_{12} = 36.8%; c, C_{10} = 53.4%; C_{12} = 46.6%; d, pure C_{12} acid. Effect of time on mixture: C_{10} = 43.8%; C_{12} = 56.2%: e, picture taken immediately; f, picture taken after 2 days; g, picture taken after 2 weeks. Sections b and c were placed incorrectly in making the illustration; they should have been reversed in position to match a and d.

TABLE III

C_{16}- C_{18} MIXTURES

Mole % C_{18}	Mole % C_{16}	Spacing with dev.	Av. spacing
100.0	0.0	39.83	39.83
89.3	10.7	39.72 ± 0.02	39.72
72.8	27.2	39.49 ± 0.04	39.49
47.5	52.5	38.50 ± 0.04	38.50
23.3	76.7	38.14 ± 0.02	38.14
9.3	90.7	35.88 ± 0.04	35.88
0.0	100.0	35.52	35.52

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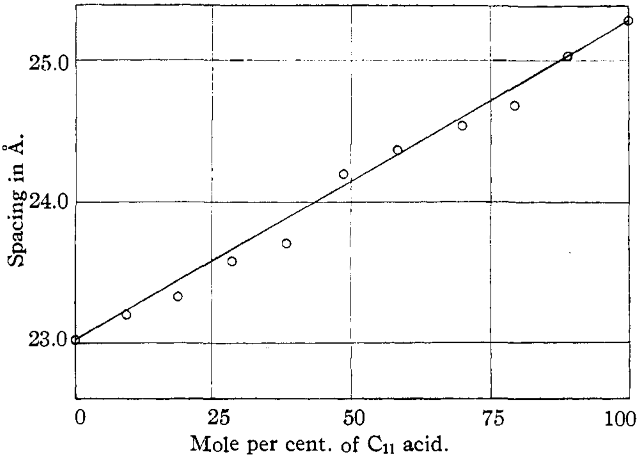
[5] S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

4. Systems with Components which Are Three Carbon Atoms Apart.—Francis, Piper and Malkin[6] report that combination spacings are obtained for equimolar mixtures of fatty acid chains of n and $n + 1$, n and $n + 2$, and n and $n + 3$ carbon atoms apart, but that equimolar mixtures of chains of n and $n + 4$ carbon atoms apart crystallize separately. They give, however, no data for such mixtures beyond the n and $n + 1$ equimolar mixtures, and fail to say anything about mixtures which are not equimolar.

In our work on mixtures of fatty acids of chain lengths n and $n + 3$ we have studied non-equimolar mixtures as well as equimolar ones. The principal studies were made on mixtures of C_{10} and C_{13} acids. The following results were obtained.



Graph I.—Mixtures of C_{10}–C_{11} acids.

(a) **Equimolar Mixture, Mole % C_{10} = 49.9; Mole % C_{13} = 50.1.**—Two separate sample plates were prepared and exposed. The spacings obtained were 26.30 Å.; 24.21 Å. and 26.29 Å.; 24.18 Å., respectively. The spacing corresponding to 24.20 Å. (average of 24.18 and 24.21) was calculated from a single first order which was very weak. As might be expected the spacing of 26.29 Å. falls on the odd acid curve corresponding to a carbon content of $11^1/_2$ carbon atoms.

(b) **Non-equimolar Mixture, Mole % C_{10} = 24.8; Mole % C_{13} = 75.2.**—Two separate samples of this mixture were prepared and exposed. Film (1) corresponds to the picture obtained from the sample which was crystallized slowly from the melt (approx. one-half minute). Film (2) corresponds to the picture obtained from the sample which was prepared by rapid crystallization from the melt (approx. two seconds). The spacings from the first case are 34.94; 28.87 and 26.36 and from the second case 34.95 and 29.59 Å.

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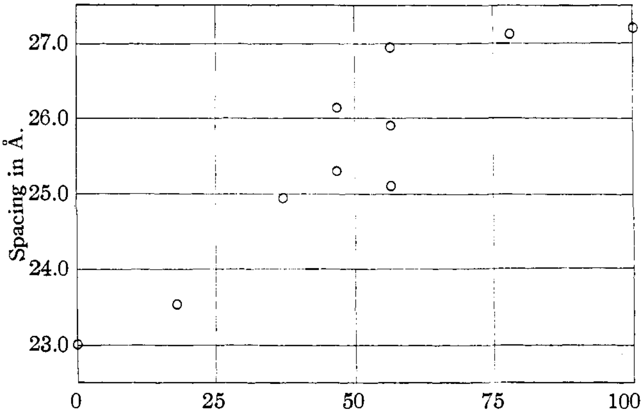
[6] F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

From the results obtained here we can see that the speed of crystallization affects the results very markedly. It is seen that the sample which was prepared by slow crystallization from the melt gave three sets of lines, all of which were of equal intensity. The sample which was prepared by rapid crystallization gave only two sets of lines, one set being weak. The set of strong lines on this second film (spacing equal to 34.95 Å.) corresponds exactly to one of the sets of lines found on the first film. The weak set of lines on this second film (spacing equal to 29.59 Å.) does not correspond to any set of lines on the first film. Thus we observe a total of four modifications in these two samples.

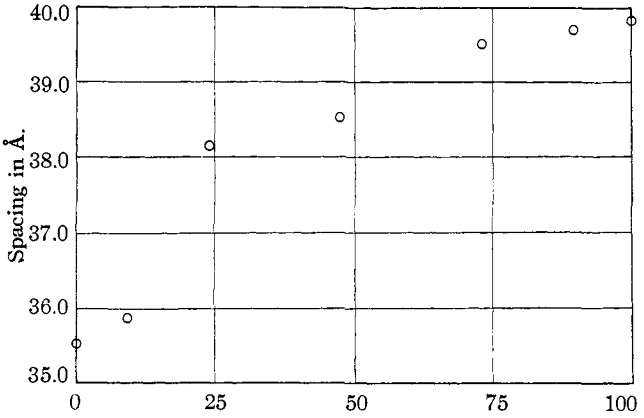


Graph II.—Mixtures of C_{10}–C_{12} acids.

(c) **Non-equimolar Mixture, Mole % C_{10} = 75.5; Mole % C_{13} = 24.5.**—A single picture was taken of the mixture. The calculations gave d = 24.64 Å. Only one set of lines is found for this mixture. The spacing obtained corresponds definitely to a mixed crystal and not to either pure acid.

For any of the three compositions listed above, mixed crystals are present since the spacings observed do not check with the pure acids. In the case of the mixture C_{10} = 75.5% and C_{13} = 24.5%, there is evidently complete mixing since there is only one phase present. In the case of the mixture C_{10} = 24.8% and C_{13} = 75.2%, we obtain a maximum of four phases. These phases represent different modifications and not phases with different composition. This is demonstrated by the fact that upon slow crystallization we obtain three phases, one of which is identical with one of the two phases obtained by rapid cooling; whereas the other is a new phase. Since the spacing corresponding to this common phase is nearly the same as the A modification for pure C_{13} acid, one might think that perhaps C_{13} crystallized out separately, leaving behind a mixture richer in C_{10}. This appears unlikely for two reasons: first, increase of speed of crystallization ought to hinder the separation of C_{13}; however, the intensity of this spacing on a sample obtained by rapid cooling shows no decrease in intensity. As a matter of fact, we find that the remaining phase (the residual mixture) from the rapidly cooled sample is present in very small amounts. In comparison with the sample with slow cooling, the sample with rapid cooling would appear to show smaller amounts of mixed crystals, which is certainly contrary to any reasonable anticipation. Second, the comparable mixture (C_{10} = 75.5%; C_{13} = 24.5%) shows complete solid solution formation only.

In the equimolar mixture we have either two phases of different composition or two phases of identical composition in different modifications. We favor the latter viewpoint in consideration of the results obtained with other mixtures, such as C_{10}–C_{12}.



Graph III.—Mixtures of C_{16}–C_{18} acids.

In addition to the C_{10}–C_{13} mixtures studied above an equimolar mixture of C_{15} and C_{18} acids (C_{15} = 49.8%; C_{18} = 50.2%) was investigated. The calculations gave spacings of 39.76 and 37.31 Å.

It is seen that this mixture gives two spacings, the values of which lie approximately half-way between the values of the proper modifications of C_{15} and C_{18} pure acids.

5. Systems with Components which Are Four Carbon Atoms Apart.—An equimolar and a non-equimolar mixture of C_{10} and C_{14} acids were used for investigations of mixtures of acids of n and $n + 4$ carbon atoms apart. The results obtained were: (a) two pictures were taken of the equimolar mixture of C_{10} and C_{14} acids (C_{10} = 50.1%; C_{14} = 49.9%). The first picture was taken immediately after the sample plate was prepared (d = 26.98) and the second picture on the same sample after two weeks had elapsed (d = 31.19).

On film (1) there was an indication of a first order (too weak to measure) of another series of lines which would give a longer spacing than the 26.98 Å. which was observed. This longer spacing would in all probability correspond to the spacing calculated from film (2). On film (2) there was not even an indication of a set of lines corresponding to the 26.98 Å. spacing, which means that the transformation to the modification with the longer spacing was complete.

It is of interest to note that according to the average composition (C_{12}) we find the spacing in the first picture close to the C modification of pure C_{12} acid (the only modification observed for this acid). It has been observed in previous cases (C_{10}–C_{12} and C_{10}–C_{13} mixtures) that such mixtures upon standing, or upon variation in speed of solidification, will change modification. In the present case a change of spacing occurs which we would like to interpret in a similar fashion. However, the new spacing observed corresponds closely to the C modification of pure C_{14}. We therefore have to consider the possibility of an unmixing of our sample. Since our original mixture has to be considered as a random arrangement it is hard to imagine that chains possessing considerable length may rearrange to form crystals containing one chain length only. Such a rearrangement, which would involve the moving about of the chains in a relatively regular crystalline arrangement, is quite different from the type of change involved in a change of modification. There, only a variation in tilt is necessary which does not affect, fundamentally, the relative position of the chain-like molecules. This latter possibility can be easily imagined to occur, and experiments show that it does occur. The first possibility appears quite unlikely and the experimental evidence seems to be against it. Namely, since we have an equimolar mixture, the formation of crystals of pure C_{14} only would by necessity give rise to the formation of crystals of pure C_{10}. This C_{10} acid would be crystallized under the conditions of the experiment. In consideration of the smaller size of the C_{10} molecules, these crystals could be formed as readily as those of C_{14}. However, although we find a spacing close to that of pure C_{14}, we find absolutely no trace of spacings that might be associated with any modification of pure C_{10}. Furthermore, if unmixing in the solid would occur, one would not expect it to be complete; so that there would remain lines corresponding to the original mixture (or one similar to it), which is in no way indicated by experimental evidence. Also if the C_{14} acid that might be separated is entirely free of C_{10} acid, the spacing observed is sufficiently different from pure C_{14} acid as to be outside the experimental error. In the still clearer case of C_{14}–C_{18} acid mixture (the data on this mixture are given below) no indication of unmixing was found at all. Thus we feel justified in claiming that the C_{10}–C_{14} mixture does not unmix in the above case, and that the new spacing observed upon standing is a new modification of the original mixture, which by chance falls close to the C modification (the only modification observed) for pure C_{14}. We have emphasized this point because similar phenomena occur in many binary mixtures of components more than four carbon atoms apart. (b) The non-equimolar mixture of C_{10} and C_{14}(C_{10} = 25.0%; C_{14} = 75.0%) upon exposure gave a picture with just one set of strong lines. There were, however, three very faint first order reflections appearing in addition. The four modifications have the following spacings: 31.27 (strong), 33.88, 28.54 and 26.96. (c) An equimolar mixture of C_{18} and C_{14} (C_{18} = 50.1%; C_{14} = 49.9%) gave the two spacings 39.05 and 35.58 Å.

Since the equimolar mixture of C_{14} and C_{18} acids has a composition equal to pure C_{16} acid, it is of interest to compare the spacings obtained in each case. The spacing of 35.58 Å. corresponds very closely to the C modification of pure C_{16} acid (which value is 35.53 Å.). Only the C modification of pure C_{16} acid was observed by us. Francis, Piper and Malkin,[6] however, report a B modification for pure C_{16} acid with a spacing of 39.1 Å.

6. Systems with Components which Are Five Carbon Atoms Apart.—For the study of mixtures of chains of n and $n + 5$ carbon atoms an equimolar mixture of C_{10} and C_{15} acids was used. Two separate sample plates were prepared and exposed and the results obtained from each are given: mole % C_{10} = 50.1; mole % C_{15} = 49.9; d = 39.62, 35.35; 28.06 and 24.98; d = 39.70, 35.44 and 27.93.

We have four modifications for this equimolar mixture. This makes the interpretation somewhat difficult, especially in view of the fact that two of the spacings correspond closely to the A and B modifications of pure C_{15} acid. In view of our previous discussions we would be inclined to believe that such coincidences are accidental and consider all four phases as different modifications only. Whether this be true or not, it is quite definite that we have at least partial mixed crystal formation, since two of the phases present give a spacing which cannot be brought into agreement with any of the known data on either pure C_{10} or C_{15} acids.

7. Systems with Components which Are Six Carbon Atoms Apart.—Two equimolar mixtures were used for the study of mixtures of chains of n and $n + 6$ carbon atoms. (a) An equimolar mixture of C_{10} and C_{16} acids (C_{10} = 49.9%; C_{16} = 50.1%) gave spacings equal to 35.31 and 29.15 Å.

Here we see that there are two sets of lines observable; the 29.15 Å. value being very close to the value that C_{13} acid would have if it fell on the even acid curve. The value of 35.31 Å. may correspond to the A modification for pure C_{13} acid. This value as found by us was 34.92 Å. Francis, Piper and Malkin[6] report a value for the A modification of pure C_{13} acid of 35.3 Å. However, it is to be noticed that this value (35.31 Å.) is close to the C modification of C_{16} acid. In view of the previous discussion, we would be inclined to believe that this coincidence is accidental, which is strengthened by the fact that C_{13} acid (which is the average of an equimolar mixture of C_{10} and C_{16} acids) does have a spacing close to this value. At any rate it is quite definite that there exists at least partial solid solution formation, since the other spacing observed (29.15 Å.) does not correspond to any known spacing for pure C_{10} or pure C_{16} acids. Similar results are indicated by the equimolar mixture of C_{12} and C_{18} acids (C_{12} = 49.9%; C_{18} = 50.1%), the spacings of which were d = 33.32, 28.81, 39.41.

Here a total of three phases is observed. Since the spacings of 33.32 Å. and 28.81 Å. cannot be fitted with any known modifications of pure C_{12} or C_{18} acids, we are certain that at least partial solid solution exists. The spacing of 39.41 Å. corresponds closely to the C modification of pure C_{18} acid but it also corresponds closely to the A modification of pure C_{15} acid (the average composition of an equimolar mixture of C_{12} and C_{18} acids), so that in this case the mixed crystal formation may be almost complete.

8. Systems with Components which Are Eight Carbon Atoms Apart.—An equimolar mixture of C_{10} and C_{18} acids (C_{10} = 49.9%; C_{18} = 50.1%) gave the spacings 31.12, 39.62 and 23.14 Å.

Here we observe three phases, two of which may be identical with the spacings of pure C_{10} and pure C_{18} acids. However, there remains a third phase which has a spacing which cannot be brought into accord with any known spacing for pure C_{10} or pure C_{18} acids. It must therefore be a solid solution of C_{10} and C_{18} acids. So here, as in any previous case, we find at least partial mixed crystal formation.

II. Complex Mixtures of Fatty Acids

In view of the fact that mixed crystals were rather easily formed for two component mixtures of acids over a wide range, it seemed to us quite probable that mixed crystals could be formed for mixtures of more than two components. Francis, Piper and Malkin[6] have shown in their interesting paper that for three neighboring acids in the fatty acid series mixed crystals are easily formed and that from such mixtures a single spacing is obtained. They, however, do not extend their experiments to include more complex mixtures. We have extended such experiments to include mixtures of as many as nine components. Four of these complex mixtures were studied.

The samples and sample plates were prepared in the same manner as described for the two-component mixtures. In all of the pictures obtained from these complex mixtures only two orders (first and third) were observable for a particular phase. The lines were somewhat broadened and the time of exposure was longer than for the two-component mixtures.

The results obtained are as follows. (1) An equimolar mixture of the even acids from C_{10} to C_{18} was studied. Three pictures were taken of this sample. The actual composition was: C_{18} = 18.9%; C_{16} = 19.0%;

C_{14} = 19.5%; C_{12} = 20.2%; C_{10} = 22.4%. For the first and third order $\sin \Theta/n = 0.01969$ (com.) and 0.01962; average = 0.01965; d = 39.15 Å. In another case $\sin \Theta/n = 0.01972$ (com.) and 0.01963; average = 0.01967; d = 39.11 Å.

Here just a single spacing was observed indicating complete solid solution formation and the check obtained on the two pictures indicates the reproducibility of the results.

This mixture was also studied by depositing the sample on the glass plate by crystallization from an acetone solution of the mixture. The calculations obtained are as follows (again for the first and third order): $\sin \Theta/n = 0.01948$ (com.) and 0.01940; average = 0.01944; d = 39.57 Å.

This picture gives one main spacing as calculated above. Also there are indicated several weak first orders of other series of lines, which appear as a band, and which correspond to spacings shorter than the one calculated, indicating partial unmixing as to be expected.

(2) An equimolar mixture of the odd acids from C_{11} to C_{17} was studied. Two pictures were taken; one picture from a sample which was prepared by rapid crystallization of the melt and the other from a sample which had slow crystallization. The actual composition of this mixture was: C_{17} = 26.4%; C_{15} = 25.3%; C_{13} = 24.0%; C_{11} = 24.3%.

(a) **Sample Prepared by Rapid Crystallization.**—For first and third order $\sin \Theta/n = 0.01951$ (com.) and 0.01941; average = 0.01946; d = 39.53 Å.

(b) **Sample Prepared by Slow Crystallization.**—For first and third order $\sin \Theta/n = 0.01906$ (com.) and 0.01901; average = 0.01903; d = 40.43 Å.; and first order of second modification $\sin \Theta = 0.02059$; d = 37.36 Å.

In this second example where slow crystallization of the sample was used we see that the sample gave two spacings (the spacing 37.36 Å. being weak and appearing in the first order only), indicating that under these conditions we obtain either two modifications or the mixed crystal formation is not complete whereas in the first case certainly complete solid solution formation is present.

(3) An equimolar mixture of all of the acids from C_{10} to C_{18} inclusive was made up and the x-ray picture taken. The actual composition of this mixture was: C_{18} = 11.1%; C_{17} = 11.1%; C_{16} = 11.3%; C_{15} = 11.3%; C_{14} = 11.3%; C_{13} = 11.3%; C_{12} = 11.1%; C_{11} = 10.8%; C_{10} = 10.7%. From first and third order $\sin \Theta/n = 0.01944$ (com.) and 0.01945; average = 0.01945; d = 39.55 Å.

Even with a mixture as complex as this one, only one spacing is observable, indicating that the mixed crystal formation must be essentially complete. (4) A non-equimolar mixture of the even fatty acids from C_{10} to C_{18} was studied. This mixture contained a larger percentage of the higher acids.

The actual composition was as follows: C_{18} = 29.8%; C_{16} = 29.2%; C_{14} = 19.6%; C_{12} = 10.4%; C_{10} = 11.0%. From first and third order $\sin \Theta/n = 0.01949$ (com.) and 0.01945; average = 0.01947; $d = 39.51$ Å.

Discussion of Results

In the interesting paper by Francis, Piper and Malkin[6] the idea was put forward that the x-ray results on equimolar mixtures of fatty acids might best be explained by assuming an arrangement in which a short and a long molecule would form a double molecule. Since double layers of molecules exist in crystals of pure fatty acids, and since always the length associated with such double molecules is measured, such an arrangement would indeed furnish a simple explanation for the fact that the spacing obtained from the mixture is the mean of the spacings of the components (provided that the proper modifications are taken). We have been inclined to consider such an explanation not adequate, since it is hard to anticipate that from a melt of the mixture such a regular arrangement could be obtained upon rapid cooling. Furthermore, since the forces holding various such molecules together in the lattice are about the same, the difference in energy of an ordered and a non-ordered crystal is small.

The experimental test gives the best answer to these questions. The suggested arrangement can only be complete in equimolar mixtures. It is, therefore, of interest to study mixtures of various concentrations. This has been done for the C_{10}–C_{11} mixtures in which it was shown that for any and every composition one definite spacing was obtained, which spacing was characteristic for a particular mixture. When such spacings are plotted against the composition it is found that the points are scattered closely around the straight line connecting the pure acids (graph I). The fact that the equimolar mixture gives the mean spacing of the two components is therefore nothing more than a special case of this more general rule. Obviously the assumption of double molecules, which has occasionally been brought forward by other chemists, is untenable. These mixtures apparently follow the similar law known for inorganic solid solutions which is expressed approximately as Vegard's rule. It is not surprising that the values are relatively widely scattered, since it has become evident in the previous discussion of the pure fatty acids that the spacings are easily affected by various influences. Similar results appear to be present in mixtures of C_{10}–C_{12} and C_{16}–C_{18}; however, in these cases the picture is complicated by the fact that various compositions do not correspond to the same modification. It appears as if two to three modifications were present, so that the points are scattered around two or three lines, one of which connects the spacings of the pure components. Similar results are obtained for the C_{10}–C_{13} mixtures. In this connection attention must be called to a recent paper[7] in which the existence of a transition point for

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[7] R. L. Shriner, J. M. Fulton and D. Burks, THIS JOURNAL, **55**, 1494 (1933).

mixtures of palmitic and stearic acid is interpreted as proof for the formation of a compound. Contrary to this view we are inclined to assume a change in modification only.

Francis, Piper and Malkin[6] indicated that solid solution does not exist in binary mixtures in which the chain length difference is more than three carbon atoms. However, we have obtained definite solid solution formation with C_{10} and C_{14} acids in two concentrations and for one concentration of C_{14} and C_{18} acids (no other concentrations were investigated). In the case of five, six and eight carbons apart it was definitely proved that at least partial solution exists in the solid state. Such mixtures had always C_{10} acid as one component, thus giving a relatively high percentage difference in chain length.

It is of interest to note that the mixtures appear to occur in a larger number of modifications than has been observed for the pure acids in this investigation.

It is a remarkable fact that for any one of the complex mixtures listed in the experimental part, a definite single spacing characteristic for one phase can be obtained. Since one phase only is obtained, this must mean that complete solid solution is present in these cases.

It is likely that the modification present in such mixtures corresponds to the one present in certain binary mixtures with large separation of chain length, namely, the ones which give the longest spacing. This may be surmised from the fact that in the case of these complex mixtures the spacing lies close to the one of the longest component. However, it must be emphasized again that this similarity of spacing cannot mean that the highest component has crystallized out, since definitely no other spacings are present in the proper samples.

In the sample which has been obtained from solution a partial separation has been observed. The spacing is slightly longer than the one obtained from the corresponding melt. Assuming identical modifications, this would mean that the main component contains more of the longer chains than would be given by the average composition, which again would necessitate the presence of phases with a higher content of the lower chains. Actually the main spacing is accompanied by a narrow weak band which must have been produced by various slightly shorter spacings.

The fact that such complex but well-defined mixtures of fatty acids give rise to well-defined reflections from the (001) plane, which interplanar distance must be associated with the chain length (although in the case of the fatty acids, due to the unknown tilt of the chains, the average chain length cannot be definitely calculated), is of special interest, since in previous investigations such an effect was claimed not to exist. Hengstenberg[8] was unable to obtain any spacings associated with the chain length

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(8) J. Hengstenberg, *Z. Krist.*, **67**, 538 (1928).

in a complex hydrocarbon mixture (the average length is not given in the reference, but judging from the title the paraffin mixture may be assumed to be C_{60}–C_{80}).

It might be argued that the average chain length was too high to be observable. With our apparatus, depending on the third order which is sufficiently strongly observed in our mixtures, we could measure spacings for a hydrocarbon mixture of average chain length of about C_{100}. It might be objected that the results obtained on the fatty acids are not applicable to other long-chain compounds. For this reason other series are being investigated. At present the preliminary results are available on several series, for which Dr. D. A. Wilson[9] observes the same effect. Since such perfect miscibility is observed for relatively short chain lengths, where the relative length differences of neighbors play a much larger role, it is reasonable to expect similar miscibility for longer chain lengths. Unfortunately such longer acids were not at our disposal in sufficiently pure form that the experimental test could be performed.

The results obtained on the mixtures of the acids are entirely non-ambiguous in their interpretation. The lines obtained are surprisingly sharp although less sharp than those obtained on the pure acids or simple mixtures. The falling off of intensities with the higher orders appears to be more rapid than in the case of the pure acids. Since these findings are so much in opposition to the prevailing opinion[10] it seems of interest to make theoretical calculations on such mixtures. This has been done by Dr. M. L. Huggins[11] in this Laboratory. His results are in perfect agreement with our experimental data.

The results obtained seem to us to be of special interest in connection with the structure of high polymers. Some such polymers are assumed to consist of chains of various lengths. If the average chain length is not excessively long, spacings connected with this average chain length should be obtained by the methods used in this work. Such effects have not been previously observed, and this has been used thus far by other workers as a criterion for the presence of chains of varying length. There is only one dissenting paper[12] in which reflections were obtained from polymer formaldehydes which were considered as lower orders of the (001) plane; since the chains are vertical to the (001) plane, the average chain length could be calculated from the data. However, at the time instead of using the concept of average chain length it seemed more cautious to consider the crystals as built up of molecules of essentially the same length only, in agreement with the prevailing opinion. Since it was more likely from chemical considerations to assume varying chain length in polymer form-

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(9) Dissertation, the Johns Hopkins University, 1933.

(10) K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, pp. 44–45.

(11) Huggins, to be published shortly.

(12) Emil Ott, *Z. physik. Chem.*, **B9**, 378 (1930).

aldehydes, Sauter[13] attacks the existence of "inner" reflections (lower orders of the (001) plane) observed by Ott. In consideration of the results obtained in this thesis, there appears to be every reason to anticipate results such as obtained by Ott on polymer formaldehydes, since the spacings observed lie in a range suitable for observation.

Summary

1. A large number of two-component mixtures of the normal fatty acids C_{10} to C_{18} have been studied. The chain length difference of the two components varied from one to eight carbon atoms. The mixtures with difference in chain length up to three carbon atoms were studied for various concentrations. In all cases mixed crystal formation was established.

2. Very complex mixtures of fatty acids (containing as many as nine components) were also measured and the existence of solid solution demonstrated.

3. These results are discussed in connection with their chemical significance.

(13) E. Sauter, *Z. physik. Chem.*, **B18**, 417 (1932).

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The Heat Capacities of Gaseous Mono- and Dimethylamine[1]

BY W. A. FELSING AND F. W. JESSEN

Object of the Investigation.—The purpose of this investigation was the experimental determination of the heat capacities of mono- and dimethylamine in the gaseous state. This study is a continuation of a series by Felsing and co-workers[2] dealing with the thermodynamic constants of monomethylamine with a view to the possible use of this substance as the refrigerating fluid in the absorption type of refrigerating units. The inclusion of dimethylamine in this study serves to present, also for the first time, heat capacity data for this substance, which itself presents possibilities as a refrigerating fluid. A study of the thermal decomposition of the methylamines yields data at elevated temperatures leading to the evaluation of their free energies of formation from the elements. Such experiments, to be reported in a later paper, have been made; to evaluate the free energy content at 25°, however, requires a knowledge of the heat capacities of these gaseous amines. These data, hence, form the objectives of this investigation.

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(1) From a portion of a thesis submitted by F. W. Jessen in partial fulfilment of the requirements for the Ph.D. degree.

(2) Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929); Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); C. T. Ashby, M. A. Thesis, University of Texas, 1931.