

The reason why the melting-point curve of the product from the second coil falls more slowly is because stearone tends to collect in the first coil, as it is less volatile than the stearic and oleic acids.

Towards the end of the operation the amount of oleic acid appears to be constant, but it is probable that some decomposition products, unsaturated in nature, are formed. This decomposition appears to be intimately connected with the unbearable smell which always becomes noticeable when the stearone is formed.

ART. LXI.—*The Association of the Fatty Acids and their Esters, and the Arrangement of Atoms in Space.*

By P. W. ROBERTSON.

[Read before the Wellington Philosophical Society, 7th October, 1903.]

IN a previous communication* were given the results of certain investigations on the association of the fatty acids in phenol solution. The work has been continued, and the normal fatty acids have been studied in greater detail. The results obtained for these compounds are given in Table I. The number of carbon atoms in the molecule is denoted by N, and A represents the rate of association of the acid

TABLE I.		
N.	Acid.	A.
2	Acetic	23
4	Butyric	14
6	Hexoic	12
8	Octoic	15
10	Decoic	28
12	Lauric	42
14	Myristic	—
16	Palmitic	80
18	Stearic	98

The rate of association of the acids with an even number of carbon atoms falls to a minimum at the sixth member, and then gradually rises with increase of molecular weight. The association of the earlier members has been shown to be due to the influence of the carboxylic group in the molecule. Some other explanation, however, must be given for the association of the higher fatty acids. An investigation of some closely related substances shows that the rapid rate of association is caused by a long chain of carbon atoms. The main grounds for this conclusion are as follows:—

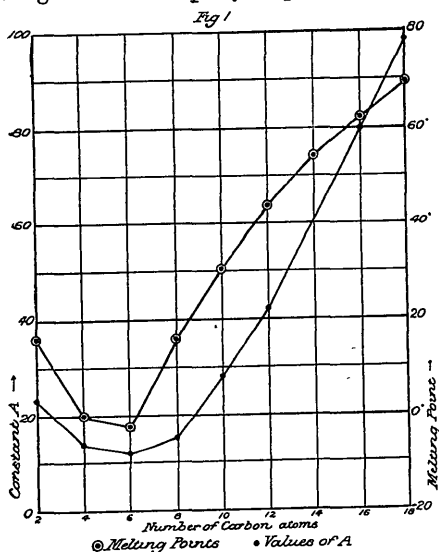
* Trans. N.Z. Inst., 1902, p. 452.

(1.) The hydrocarbons themselves associate rapidly in phenol solution.

(2.) The ethereal salts of the lower fatty acids have a negative value for A , and show little or no association. But ethyl laurate and ethyl palmitate associate rapidly, and the association is greater for the compound with the longer carbon chain.

(3.) The introduction of an ethylene linkage in stearic acid breaks the continuity of the hydrocarbon chain, and the rate of association is considerably reduced.

(4.) Amongst the lower fatty acids—butyric acid, for example—the introduction of a bromine atom in the α position to the carboxyl reduces A to about half its original value; higher up the series this is not the case, a bromopalmitic acid associating almost as rapidly as palmitic acid itself.



Various other properties of the fatty acids show a minimum or maximum at the sixth member. The most characteristic example is furnished by the melting-points. These are graphically depicted with the values of A in fig. 1. The minimum is reached in both cases at the same acid, and the similarity between the two curves is readily noticeable. These results show clearly to what an extent the melting-point of a substance is dependent on its association. Further, they confirm the conclusion already arrived at*—namely, that “a maximum or minimum of a series is due to the molecular complexity of one or more members of that series.”

* Trans. N. Z. Inst., 1902, p. 465.

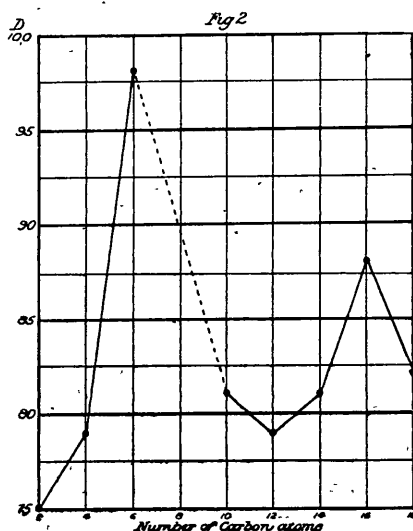
Some closely connected law seems to regulate the distribution of the fatty acids in nature. A rough analysis of the fatty acids obtained by the saponification of cocoa-butter showed that the compounds were present in the following proportions:—

Butyric acid (C_4)	2 per cent.
Hexoic acid (C_6)	0 "
Octoic acid (C_8)	1 "
Decoic acid (C_{10})	4 "
Lauric acid (C_{12})	50 "

Here again it is the sixth member which occurs to the smallest extent.

Though smell is a property concerning which little is known, yet it does not seem entirely devoid of interest to mention that of all the even fatty acids hexoic acid has the most repugnant odour. Thus it seems as if, in the case of the cocoa-tree, the most offensive acid is prepared in the least quantity by the plant.

A study of the cyoscopic behaviour of the normal fatty esters in phenol solution gives somewhat similar results, in that it is again at the sixth member that a sudden change is exhibited. In the case of these compounds, however, there is also a change of the opposite nature at the compound with twelve atoms. This appears to be the first instance known of the regular occurrence of both a maximum and minimum in the same series of compounds.



The data for the even members of the normal fatty esters are given in Table II. D represents the initial molecular depression for a fall of 0.5° .

TABLE II.

N.	Ester.	D.
2	Ethyl acetate	75
4	Ethyl butyrate	79
6	Ethyl hexoate	98
8	Ethyl octoate	—
10	Ethyl decoate	81
12	Ethyl laurate	79
14	Ethyl myristate	81
16	Ethyl palmitate	88
18	Ethyl stearate	82

The values of D are plotted against N (the number of atoms in the acid portion of the molecule) in fig. 2. The resulting curve shows a minimum and two distinct maxima.

According to Baeyer's tension theory a chain of six carbon atoms bends round to form a ring in space. But, as shown above, there is a considerable tendency for the formation of maxima or minima in the case of compounds with a chain of six and twelve carbon atoms. Hence it appears that association, which has been shown to cause the appearance of a maximum or minimum, is largely influenced by the arrangement of the atoms in space. Further, the regular rise and fall in the properties of the esters of the fatty acids can be explained on the assumption of Baeyer's hypothesis of the configuration of a chain of carbon atoms in space.

ART. LXII.—*A Flash of Lightning.*

By Archdeacon WALSH.

[Read before the Auckland Institute, 12th September, 1904.]

ABOUT last February a thunderstorm passed over the district of Taiamai, a tract of volcanic country lying about half-way between the Bay of Islands and Hokianga. The discharges were not very frequent, but were unusually heavy. One of them fell in a fairly level paddock close to the coach-road from Ohaeawai to Kaikohe, about half a mile from the former place. A wagon drawn by a team of horses was passing at the time, when the horses, terrified by the blinding flash, bolted, and the wagon was upset. It was raining in torrents, and a couple of Maoris, who were standing under the verandah of a cottage some three or four hundred yards off, stated that the