297. *The Heats of Crystallisation of Methyl and Ethyl Esters of Monobasic Fatty Acids.*

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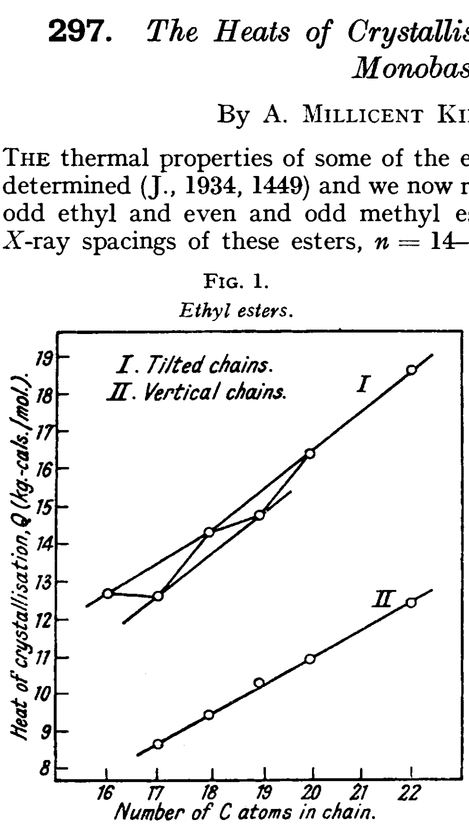
The thermal properties of some of the even ethyl esters, $n = 12$—30, have already been determined (J., 1934, 1449) and we now report an investigation into the properties of some odd ethyl and even and odd methyl esters. Malkin (J., 1931, 2796) investigated the X-ray spacings of these esters, $n = 14$—26, at room temperature, and showed that the ethyl esters occur both as tilted, 67° 30′, and as vertical forms, and in both cases probably as single molecules. The tilted forms give an alternating and the vertical forms a non-alternating series, as is clear from Malkin's X-ray spacings and also from our heats of crystallisation (Fig. 1). Up to $n = 20$ or 22, the tilted form has the higher m. p. and hence is the stable form in contact with the melt, whereas the vertical modifications of the even ethyl esters are stable above $n = 22$. On the other hand, for the odd ethyl esters, $n = 17$ and 19, the vertical forms are in equilibrium with the liquid. Thus the switch over, in the relative stabilities of the vertical and the tilted modifications, occurs at a higher chain length for the even than for the odd ethyl esters.

Fig. 1.

Ethyl esters.



The forms of the methyl esters obtainable at room temperature show an interesting phenomenon. The even esters give only one series, consisting of double molecules with an angle of tilt of 63° (from solvent and from the melt), whereas the odd esters give double molecules with an angle of tilt of 67·5° (from solvent) and also a metastable form consisting of single molecules with an angle of tilt of 75° (Malkin, *loc. cit.*). Our thermal measurements, in agreement with the X-ray measurements, show that the even methyl esters give only one form from the melt, and that this has the properties of a tilted form ($\Delta_{\mathrm{CH}_2} = 1{\cdot}08$

kg.-cals.; specific heat of solids = 0·43 cal./degree), and must be that of Malkin with an angle of tilt 63° and with the molecules arranged in pairs in the crystal. Only one odd methyl ester (C_{19}) has been examined, and this gives two forms, one coming out from the melt and passing into the second form 8° below the m. p. That stable at room temperature probably possesses an angle of tilt of 67·5° and may be composed of double molecules. The form coming out from the melt may be Malkin's metastable form. Since, however, the specific heat of this form of the methyl ester is abnormally high, *viz.*, 0·62 cal./g., it is probably a vertical form with the hydrocarbon chains in oscillation.

It would be expected that the transition from the vertical to the tilted forms would possess very different characteristics in the case of the ethyl and methyl odd esters, since, according to the *X*-ray data, the transition for the ethyl esters occurs without any change in the degree of association, whereas for the methyl esters the transition is from single to double molecules. The heats of crystallisation and transition in the two cases, for the ethyl and methyl esters of the C_{19} acid (Table I), are, however, practically identical, and this fact is difficult to understand in terms of Malkin's conclusions from the *X*-ray data. From the thermal data, it would appear that the transitions for the ethyl and methyl odd esters are very similar processes.

TABLE I.

Heats of Crystallisation and Transition, Specific Heats, and Transition Temperatures of Esters.

No. of C atoms in chain.	Heat of crystn. (kg.-cals./g.-mol.).		Heat of transtn. (kg.-cals./g.-mol.) at s.p.	Sp. heats (cal./g.).	Solid.		Transtn. temp.	
	V.*	T.*		Liquid.	V.	T.	V ⟶ T.	S.p.
Methyl.								
14	—	10·63 †	—	0·53	—	0·48	—	18·35°
16	—	13·23	—	0·52	—	0·44	—	29·05
18	—	15·40	—	0·51	—	0·43	—	37·78
20	—	17·62	—	0·52	—	0·42	—	45·41
22	—	19·68	—	0·54	—	0·42	—	51·84
19	10·24	14·87 ‡	4·63	0·51	0·62	0·45	31°	38·64
Ethyl.								
17	8·66	12·62	3·96	0·50	0·76	0·44	18	25·15
19	10·32	14·74	4·42	0·50	0·64	0·46	27	36·05

* V = Vertical form; T = tilted form.

† Garner and Rushbrooke, J., 1927, 1351. ‡ Double molecules in crystal.

A summary of the thermal properties of the esters investigated is given in Table I. The melting points of the even methyl esters are given by

$$T = (1{\cdot}083n - 4{\cdot}15)/(0{\cdot}002839n - 0{\cdot}00185) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and of the odd ethyl esters by

$$T = (0{\cdot}8389n - 5{\cdot}58)/(0{\cdot}00224n - 0{\cdot}00904) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the agreement between the theoretical curves and the experimental m. p.'s is seen in Table II. The bearing of these results on those of other homologous series is discussed in the preceding paper, where the plot of the entropies of the even methyl esters is also given.

EXPERIMENTAL.

Kahlbaum's purest palmitic and stearic acids were used in the preparation of the corresponding methyl esters. The acid was esterified with sulphuric acid and methyl alcohol, and the ester distilled in a vacuum and recrystallised to constant m. p. from distilled methyl alcohol. The methyl esters of eicosoic and behenic acids were prepared from the corresponding ethyl esters already described (J., 1934, 1449) via the potassium salt and the acid. Ethyl nonadecoate was prepared by esterification of 10 g. of the acid which had been carefully purified by Dr. F. J. E. Collins and was kindly given to us by Professor Francis, who also supplied us with a pure specimen of ethyl margarate, obtained from the acid previously described (J., 1929, 1857). Methyl nonadecoate was obtained from the ethyl ester in the manner described for methyl eicosoate. The setting points of these very pure esters, together with those calculated for the methyl esters from equation (1) and for the odd ethyl esters from equation (2), are given in Table II.

TABLE II.

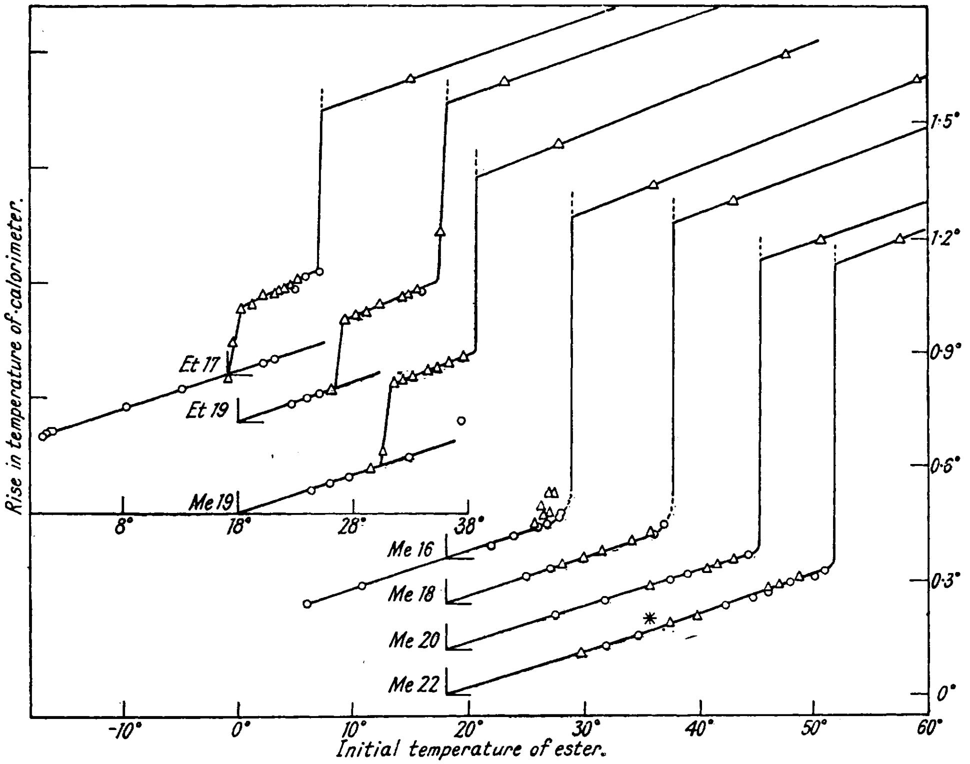
Calculated and Observed Setting Points of Esters.

No. of C atoms in chain.	Methyl esters. S. p., calc.	S. p., obs. T.	Δ.	Ref.	Ethyl esters. S. p. calc.	S. p. obs. V.	Δ.	Ref.
10	251·7°	255°	+ 3·3°	—	—	—	—	—
12	274·4	278	+ 3·6	—	—	—	—	—
14	290·5	291·4	+ 0·9	G.R.	—	—	—	—
15	—	—	—	—	285·1°	285°	− 0·1°	P.M.
16	302·5	302·1	− 0·4	K.G.	—	—	—	—
17	—	—	—	—	299·0	298·2	− 0·8	K.G.
18	311·4	310·8	− 0·6	K.G.	—	—	—	—
19	—	311·6 *		,,	309·1	309·1	0·0	K.G.
20	318·7	318·4	− 0·3	K.G.	—	—	—	—
21	—	—	—	—	317·0	318 †	+ 1·0	L.T.
22	324·5	324·8	+ 0·3	K.G.	—	—	—	—

K.G. = King and Garner, present research. P.M. = Phillips and Mumford (J., 1934, 1658).
L.T. = Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905). G.R. = Garner and Rushbrooke, *loc. cit.*
* Probably vertical form. † Indicates m. p.

Procedure.—The method of determining the specific heats and heats of crystallisation was exactly the same as that employed in work with the acids, hydrocarbons, and even ethyl esters (*loc. cit.*), and the same calorimeter was used. Table III contains only the data essential for calculation of the specific heats and heats of crystallisation, but the complete experimental data are shown graphically in Fig. 2. As in previous work, points marked △ represent

FIG. 2.



experiments in which the molten liquid was allowed to crystallise in the thermostat at the temperature of the experiment, and those marked ○, experiments in which the ester was solid when it was placed in the thermostat.

TABLE III.

Methyl palmitate (setting point = 29·05°).

(Wt. of ester, 5·390 g.; glass, 5·835 g.; platinum, 0·1217 g.)

Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.	Expt. No.	Initial temp. of ester.	Fall in temp.	Rise in temp.
2	23·95°	6·17°	0·063$_8$°	7–9	59·07°	40·94°	1·248$_2$°
4—6	36·09	18·81	0·985$_0$				

σ_{S_T} = 0·4378 cal./g.; σ_L = 0·5243 cal./g.; Q = 13·23 kg.-cals./g.-mol.

Methyl stearate (setting point = 37·78°).

(Wt. of ester, 5·215 g.; glass, 5·873 g.; platinum, 0·1327 g.)

1	27·17	8·70	0·087$_4$	15—17	65·57	46·88	1·302$_0$
10—14	43·16	24·92	1·051$_9$				

σ_{S_T} = 0·4317 cal./g.; σ_L = 0·5077 cal./g.; Q = 15·40 kg.-cals./g.-mol.

Methyl eicosoate (setting point = 45·41°).

(Wt. of ester, 4·770 g.; glass, 5·690 g.; platinum, 0·1324 g.)

1	27·66	9·78	0·090$_5$	14—16	76·49	58·22	1·352$_4$
9, 11, 13	50·57	32·25	1·071$_4$				

σ_{S_T} = 0·4235 cal./g.; σ_L= 0·5220 cal./g.; Q = 17·62 kg.-cals./g.-mol.

Methyl behenate (setting point = 51·84°).

(Wt. of ester, 4·942 g.; glass, 5·698 g.; platinum, 0·1340 g.)

1	34·82	17·45	0·164$_0$	11—13	81·58	63·53	1·462$_7$
6, 7, 10	57·62	39·41	1·190$_8$				

σ_{S_T} = 0·4166 cal./g.; σ_L = 0·5360 cal./g.; Q = 19·68 kg.-cals./g.-mol.

Ethyl margarate (setting point = 25·15°).

(Wt. of ester, 4·856 g.; glass, 5·885 g.; platinum, 0·1246 g.)

39	13·07	4·25	0·041$_3$	8—10	33·00	22·71	0·840$_9$
23	18·25	7·79	0·244$_7$				
28	23·91	13·72	0·329$_1$	13—15, 30	54·51	44·18	1·069$_1$

σ_{S_T} = 0·4433 cal./g.; σ_{S_V} = 0·7645 cal./g.; σ_L = 0·4969 cal./g.;
Q_T = 12·62 kg.-cals./g.-mol.; Q_V = 8·66 kg.-cals./g.-mol.

Heat of transition V $\longrightarrow$ T = 3·96 kg.-cals./g.-mol.

Ethyl nonadecoate (setting point = 36·05°).

(Wt. of ester, 4·871 g.; glass, 5·617 g.; platinum, 0·1340 g.)

2	25·11	7·93	0·078$_8$	7—9	41·17	23·64	0·886$_7$
18	33·62	15·54	0·340$_7$	10, 13, 14	63·77	45·11	1·114$_7$
21	29·07	10·69	0·279$_9$				

σ_{S_T} = 0·4648 cal./g.; σ_{S_V} = 0·6349 cal./g.; σ_L = 0·5008 cal./g.;
Q_T = 14·74 kg.-cals./g.-mol.; Q_V = 10·32 kg.-cals./g.-mol.

Heat of transition V $\longrightarrow$ T = 4·42 kg.-cals./g.-mol.

Methyl nonadecoate (setting point = 38·64°).

(Wt. of ester, 4·970 g.; glass, 5·575 g.; platinum, 0·1340 g.)

14	29·40	11·91	0·117$_5$	5, 6, 8	43·91	26·11	0·961$_3$
10	34·41	16·66	0·372$_0$	12, 13, 17	65·62	47·83	1·196$_4$

σ_{S_T} = 0·4517 cal./g.; σ_{S_V} = 0·6152 cal./g.; σ_L = 0·5079 cal./g.;
Q_V = 10·24 kg.-cals./g.mol.; Q_T = 14·87 kg.-cals./g.-mol.

Heat of transition V $\longrightarrow$ T = 4·63 kg.-cals./g.-mol.

It will be noted that only a tilted form is obtained for the methyl even esters, although near the m. p. of methyl palmitate, irregular results are obtained which might have been evidence of a vertical form had they not been equally well explained by the slow rate of crystallisation of the lower esters near their m. p.'s (Fig. 2). A curious feature of methyl eicosoate is that no solidification is obtained when the ester is kept for 10 hours at a temperature 1½° below the m. p. The solid ester, kept for 4 hours at a slightly higher temperature, however, gives the normal heat content, showing that no melting occurs at this temperature.

In the case of methyl behenate, the tilted form near the m. p. seems to be definitely different from that at room temperature, the phase change taking place at *ca.* 36° (* on Fig. 2). A similar phase change at 30° had previously been observed with ethyl behenate (Buckingham, *Trans. Faraday Soc.*, **1933**, **30**, 377). The methyl C_{19} ester exists in two forms, one probably vertical and the other tilted, the transformation from one into the other being irreversible. The vertical passes into the tilted form on cooling, but the reverse change does not occur up to within 1° of the m. p.

SUMMARY.

The specific heats and heats of crystallisation of the following esters of the straight-chain fatty acids have been measured: methyl, C_{16}, C_{18}, C_{20}, C_{22}, and C_{19}; ethyl, C_{17} and C_{19}. Two equations have been derived connecting the melting points with the number of carbon atoms in the chain, for the methyl esters of the even series and the ethyl esters of the odd series, severally.

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