III.—THE SOLIDIFYING POINTS OF BINARY MIXTURES OF FATTY ACIDS AND ESTERS.

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A knowledge of the solidifying point of binary mixtures of fatty acids or of their esters is of value for determining the proportion of the constituents in mixtures such as those obtained while fractionating a mixture of esters during the investigation of an oil. (*Cf.* Patel, Sudborough & Watson, *J. Indian Inst. Sci.*, 1923, **6**, 120.) The solidifying point of a mixture being much more sharply defined than the melting point, gives more accurate results than those which can be obtained by determining the latter property, but apart from measurements made in this laboratory very few data appear to exist except the figures for palmitic and stearic acid of de Visser (*Rec. trav. chim.*, 1898, **17**, 182).

In addition to their value for analytical purposes, solidifying point curves should give information regarding the state of molecular aggregation of the constituent substances, a problem of some complexity where the fatty acids are concerned. We have consequently made determinations for several mixtures and have compared the results with those previously obtained in this laboratory and elsewhere.

EXPERIMENTAL.

PREPARATION OF MATERIALS.

Acetic acid.—The purest commercial sample obtainable was fractionally distilled four times, the middle fraction twice partially frozen and the crystals separated, great care being taken to exclude moisture during the whole of the operations. In spite of this there appears to have been slight contamination as the product solidified at 16·4°, 16·7° being the accepted value.

n-*Butyric acid.*—A pure specimen was fractionally distilled 3 times yielding a product boiling sharply at 163° and solidifying at –8·1°.

Capric acid.—A synthetic specimen was fractionated and the middle fraction boiling at 136° at 5 mm. recrystallized 12 times from absolute alcohol. The product melted at 31·4° the accepted value, but the solidifying point was only 30·9°.

Methyl laurate and methyl myristate were prepared from fairly pure samples which had been made by fractionation of the methylated fatty acids from hydrogenated *Salvadora oleoides* (*cf.* Patel, Iyer, Sudborough and Watson, *J. Indian Inst. Sci.*, 1926, **9**A, 117). The solidifying points of these preparations were 2·5° and 14·5°. Attempts at purification by freezing were not successful and consequently the esters were fractionated at 7 mm. pressure through a four-bulbed column filled with Lessing rings. After four distillations the methyl laurate boiled within 1° and its solidifying point remained unchanged at 4·4° on refractionation. The methyl myristate required only two distillations to reach a steady solidifying point 15·9°.

Lauric and myristic acids were prepared from the purified esters by saponification with alcoholic potash and recrystallized twice from alcohol. Their solidifying points were 43·5° and 53·0°, respectively. In spite of the apparent purity of its ester, the solidifying point of the myristic acid was low, 53·8° being a better value. (*cf.* Joglekar and Watson, *J. Indian. Inst. Sci.*, 1930, **13**A. 119.)

Stearic acid.—A pure sample was recrystallized five times from 95 per cent. alcohol and the last traces of solvent removed by heating to 50° in a vacuum for some hours. The solidifying point was 69·2°.

Lignoceric acid from *Adenanthera pavonina* was twice ground with acetone and the liquid separated by suction in order to remove lower acids. The solid portion was then crystallized twice from toluene and three times from carbon disulphide. The product melted sharply at 80·8° but the solidifying point was only 79·3°. It may be mentioned that this acid is not *n*-lignoceric acid which melts at 80·5°, but appears to have a side chain, the position of which is under investigation.

DETERMINATION OF SOLIDIFYING POINTS

Solidifying points were determined by the usual method of observing maximum temperature reached by the molten substance on solidification. Temperatures were measured with thermometers divided to 0·2° or 0·1° and calibrated against standards.

For temperature control, a bath of calcium chloride solution was used above 10° and ice or a freezing mixture of ice and salt down to −15°. Between −15° and −25° calcium chloride hexahydrate and ice were found suitable and for still lower temperatures the vessel to be cooled was suspended in a tall vacuum vessel with a small quantity of liquid air at the bottom. In all cases the test tube containing the substance was surrounded by a wider one to form an air jacket. In the case of mixtures liquid at room temperature, stirring was effected with a magnetic stirrer to avoid condensation of moisture. Numerous experiments were made with different quantities of material, different bath temperatures and different degrees of supercooling. It was found that results reproducible to 0·1° could be obtained with 3 grams of material provided that the bath temperature was maintained not more than 2 or 3 degrees below that of the melt and supercooling was not excessive (about 2 degrees). All mixtures were made by adding successive weighed quantities of one constituent to the other; those containing approximately 50 per cent. of each constituent were thus arrived at in two ways, by adding A to B, or B to A, and a considerable overlap was usually allowed between the two series.

The following tables give values for the solidifying points of different mixtures, and Figs. I and II show the shape of the curves obtained on plotting these points against the percentage compositions of the mixtures. The points marked show composition by weight and the second curves drawn in several cases refer to molecular proportions. In both tables and curves, a small correction has been applied where necessary to bring the solidifying points of the pure acids to their accepted values:—

TABLE I.

Solidifying points of binary mixtures of acids and esters.

Percentage weight of first-named compound	Behenic —stearic	Lauric —stearic	Capric —stearic	Lauric —lignoceric	Lauric —myristic	Butyric —acetic	Me-laurate —me-myristate
100	79·3	43·5	31·0	43·5	43·5	— 8·1	4·4
90	76·9	38·6	26·6	43·8	39·3	—16·2	0·4
80	74·4	38·3	35·6	51·5	36·0	—24·5	—2·8
70	71·7	41·5	43·8	58·2	33·8	—33·0	—4·8
60	68·5	47·9	49·5	63·0	35·7	—28·6	—2·2
50	64·8	53·1	53·9	66·6	36·4	—18·2	1·0
40	63·6	57·9	57·4	69·5	39·2	— 8·2	4·1
30	62·3	61·6	60·8	72·2	43·3	— 1·6	7·2
20	63·0	64·5	63·7	74·6	47·0	5·0	10·4
10	65·2	67·0	66·6	76·9	50·6	11·0	12·5
0	69·3	69·3	69·3	79·3	53·8	16·7	15·9

De Visser's figures for palmitic and stearic acids and those for the pairs methyl palmitate-methyl stearate and methyl stearate-methyl behenate which have been published previously (*J. Indian Inst. Sci.*, 1923, **6**, 120 and 1926, **9**, 69) are not given in the table, but the corresponding curves are shown for the sake of comparison.

It will be noticed that the curves for all the acids are of a similar type. Starting with the higher melting acid the curvature is concave towards the X-axis. A break then occurs which appears to be more pronounced the closer the acids are to each other in the homologous series. Lauric and myristic acids are the only two exhibiting a definite minimum; palmitic and stearic acids have a distinct flat portion in the curve; the curves for stearic-lauric and stearic-behenic acids tend to become flat, while in the case of the others a fairly well-defined break alone is observable. After reaching a eutectic point the curves rise and are convex to the X-axis.

If the curves showing molecular percentage are examined it is seen that although the flat portion for the pairs stearic-behenic, stearic-palmitic and lauric-myristic acids corresponds very nearly to the equimolecular mixture, in no case do the two coincide. The nearest approach is shown by the last mentioned pair for which a maximum occurs at 53 mols. per cent. of lauric acid. Compound formation is thus in all probability best defined with these two acids. When the quantity of compound is relatively small, the flat portion appears when the molecular proportion of lower-melting acid is greater than 50 per cent. i.e., 60 per cent. of stearic when mixed with behenic acid and 57 per cent. of palmitic when mixed with stearic acid. For the lauric-stearic acid mixture the curve indicates a compound at about 80 per cent. of the former acid or 4 mols. to 1, while with capric and stearic acids, the ratio is still higher. It is not possible to decide whether compounds of this nature are really formed or whether the bend in the curve is displaced owing to the fact that compound formation is incomplete and that a ternary mixture of unknown composition is being dealt with.

The curves for the esters are of the simple eutectic type, methyl palmitate and stearate being the only pair with a definite break while the small inflection for methyl laurate and myristate may be due to experimental error.

The depressions in the solidifying points of pure acids on the addition of a second substance might be expected to yield data of some interest, but the results are so irregular that no deductions can be made without further experimental values. Table II gives Δ, the depression which would be produced by 100 g. of acid dissolved in 100 g.

Fig. I

Solidifying points of binary mixtures with stearic acid

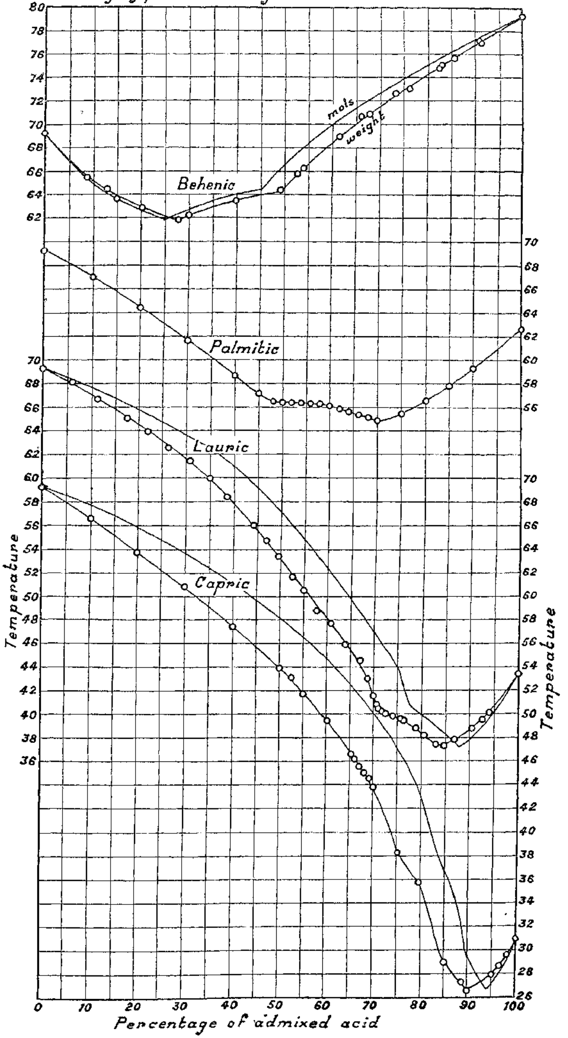
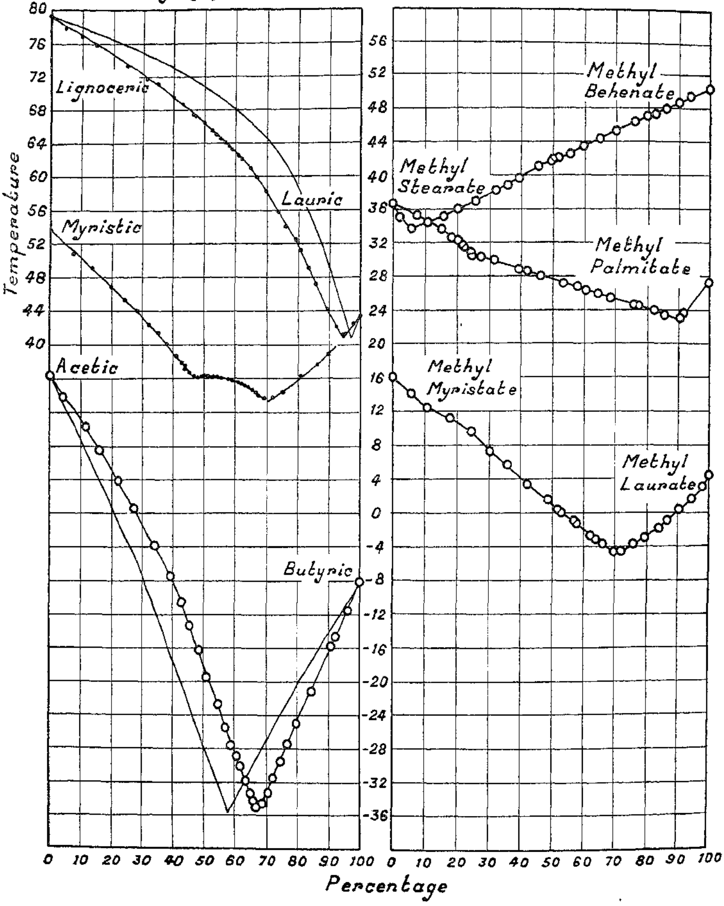


Fig. II

Solidifying point curves of acids and esters



of solvent acid if it were proportional to the depression when very small quantities were added, and *K* the depression produced by 1 gram molecule of dissolved acid with a similar assumption, *K* being thus the usual cryoscopic constant. The values are derived from the initial slopes of the curves and are necessarily very approximate.

TABLE II.

Depressions of solidifying points.

Solvent.	Solute.	Δ.	*K*.	Solvent.	Solute.	Δ.	*K*.
Stearic	Capric	24	41	Lignoceric	Lauric	23	46
Stearic	Lauric	23	46	Behenic	Stearic	24	68
Stearic	Palmitic	21	54	Palmitic	Stearic	35	100
Stearic	Behenic	45	155	Myristic	Lauric	32	64
Lauric	Myristic	40	90	Capric	Stearic	68	195
Lauric	Stearic	56	160	Butyric	Acetic	85	52
Lauric	Lignoceric	40	148	Acetic	Butyric	52	46
Me. stearate	Me. palmitate	18	48	Me. palmitate	Me. stearate	48	140
Me. stearate	Me. behenate	52	185	Me. behenate	Me. stearate	18	53
Me. myristate	Me. laurate	27	58	Me. laurate	Me. myristate	46	112

The only definite feature of these results is that for the higher acids and esters the depression produced by adding a substance of higher melting point than the solvent is very much greater than when the added substance has a lower melting point. The values of *K* for the same acid are by no means constant, but, judging from the stearic acid figures, seem to rise with rise in the molecular weight of the added acid. Δ, on the other hand, is not far from 23 when the added acid has the lower melting point and is in the neighbourhood of 40 when the converse is the case. This fact may be utilised as a very rough method of estimating the amount of impurity in an acid undergoing a process of purification but is of no value for quantitative work unless the impurity is a known acid. The cryoscopic constant has been determined by Eykman (*Z. physikal Chem.*, 1889, **3**, 203; **4**, 497) for capric, lauric, palmitic and stearic acids by dissolving naphthalene, benzophenone and anethol in them, the values being 47, 44, 44 and 45 respectively. His acids with the exception of lauric were very impure as shown by their solidifying points and consequently the results are not entirely reliable. More recently, Stratton and Partington (*Phil.*

Mag. 1924, (6) 48, 1085), have found the value 43·13 for palmitic acid. These figures show that the values of K obtained when the dissolved acid has the lower melting point are approximately normal and that the high values are abnormal. The value of K for acetic acid is higher than the true cryoscopic constant which is 39 but no deductions can be made until further experimental values for pairs of lower acids are available. These will be determined shortly and may lead to more definite results.

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