minous transmission correlates better with oil and shortening appearance than does Lovibond red readings. The committee believes that this work should be continued with the idea in mind that ultimately a simple photometric device could be evolved for the grading of oils.''

The chairman of the committee would like to add, however, that the subcommittee has done a very large amount of valuable work which is a real contribution to the colorimetry of vegetable oils and takes this opportunity of thanking them for it.

G. WORTHEN AGEE, *Chairman.*

Melting Points of Binary Fatty Acid Mixtures C_6 to C_{12} and Their Application in the Determination of Purity

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TECHNOLOGICAL progress is creating a demand for individual fatty acids in high purity. The literature contains considerable information on the determination of the purity of acids C_{12} or higher, but there is a lack of data of this type for the naturally occurring acids C_6 to C_{12}. It is the purpose of this paper to present data by which the purity of these lower acids may be readily established.

Most of the physical or chemical constants of fatty acids, such as saponification value or refractive index, are valuable in themselves only in the estimation of average molecular weights or the composition of binary mixtures. In the case of binary mixtures having a high concentration of one acid, the determination of this acid by such methods lacks precision. This is truer of ternary mixtures of this type, in which case the sample must be resolved into binary mixtures as in fractional distillation.

Twitchell (1) and Wenzel (2) have demonstrated that the melting point is a valuable tool in determining the fatty acid composition of stocks of the tallow class. Schuette and Vogel (3) reported the solidification points of binary acid mixtures C_{10} to C_{24}. Both constants are useful in assaying purity since they afford a means of determining total impurities with accuracy when present in amounts up to 20%. By either method, purity may be determined precisely by difference.

For use in analysis and control, the melting point has the advantage of faster examination of multiple samples in standard equipment, using familiar techniques. In the case of the lower acids, melting point depression is linear over a longer range of solute concentration and the determination is made at higher and more easily controlled temperatures, since mixtures of the lower acids supercool more than higher members of the series.

Data in this study were obtained by preparing samples of pure caproic, caprylic, capric and lauric acids and determining the melting points of binary mixtures of adjacent acids.

Preparation of Pure Fatty Acids

COCONUT oil fatty acids was the source from which a low-boiling fraction containing the acids C_6 to C_{12} was separated by continuous rectification under vacuum. This fraction was separated by batch rectification into four cuts, each rich in one of the acids. Each cut was further purified by successive vacuum distillations, using a Vigreux column until a product was obtained having the proper boiling point and a melting point not more than 0.2°C. lower than the best reported value.

Final purification was obtained by successive recrystallizations from acetone until no increase in melting point was observed. Each acid crystallized well from this solvent in white leaves or needles at —55°C. for caproic acid, —30°C. for caprylic acid and 5°C. for capric and lauric acids. Last traces of solvent were removed by heating gently under high vacuum.

The following melting points were obtained on the pure acids:

Acid	Observed M.P.°C.	Reported M.P.°C.	Reference
Caproic	—3.4	—3.9	(4)
Caprylic	16.7	16.5	(5)
Capric	31.6	31.6	(3)
Lauric	44.2	44.2	(3)

The melting point of these acids is in agreement with best reported figures. It is true that Beilstein, quoting Fittig (6), gives —1.5°C. as the melting point of *n*-caproic acid, but this has not been confirmed in recent literature, and it is probable that the acid examined by Fittig is an isomeric acid, 2-3-dimethyl butanoic acid which has a melting point of —1.5°C., determined by Hommelen (4).

Melting Point Determination

THE equipment used is essentially that described by Wenzel (2). It can be assembled on short notice in any well-equipped laboratory. It consists of a one-liter Pyrex beaker three-quarters full of water or alcohol heating fluid, kept in rapid circulation by a motor-driven glass agitator. Above 0°C., water is used and the temperature is increased at the desired rate by a micro bunsen burner. For below zero temperatures, alcohol chilled with dry ice is employed and the beaker is insulated except for an observation space. Heat is absorbed from the atmosphere augmented by the micro burner. A microscope lamp provides illumination.

The thermometer has a range of —36° to 54°C., graduated in 0.2° units. Readings to less than 0.1°C. are readily made by the use of a magnifying attachment. The thermometer is calibrated in the range 0 to 50°C. against a titer thermometer certified by the Bureau of Standards and at the melting point of recrystallized carbon tetrachloride, —22.9°C. It is checked frequently at the ice point.

Pure acids in the proportion desired are weighed to 0.1 mg. in a small vial to give a sample of about one gram. A three-centimeter column of the liquid mixture is drawn into the melting point tube by capillarity and the ends of the tube sealed. The melting point tubes are drawn from soft glass and have inside diameters of 0.64 to 0.74 mm. as determined by acceptance of fine wires of these sizes. As many as ten tubes are fastened in a vertical position by rubber bands to a light stick similarly fastened to the thermometer at the liquid level and the immersion point of the thermometer. The samples in the tubes are chilled in the apparatus to at least 20°C. below the melting point. The temperature of the heating fluid is increased rapidly to within 5°C. of the melting point and then at the rate of 0.2°C. per minute until the last trace of solid is melted in the tube. This is taken as the melting point and is most readily observed by transmitted rather than reflected light.

Results

THE results of the melting points of three pairs of binary mixtures included in this study are presented as melting point versus weight and mol per cent of the higher melting component in Table I and are also shown graphically in Figures 1 and 2.

The melting point-composition relation for each binary mixture as shown graphically may be divided into three smooth curves intersecting at a minimum and at an incongruent melting point. The minimum melting points occur between 26 and 28 mol per cent of the higher melting component and the incongruent melting points between 40 and 47 mol per cent.

In all cases studied, the melting point depression is linear up to solute concentrations of 20 weight per cent. The specific depression constants in this range are given in Table II in which Km is melting point depression in °C. per mol per cent solute and Kw is given in °C. per weight per cent solute.

With C_8 as solvent, the molal melting point depression constant, Km, is identical for C_6 and C_{10} solute acids. For C_{10} as solvent, the difference in Km for C_8 and C_{12} solutes is small.

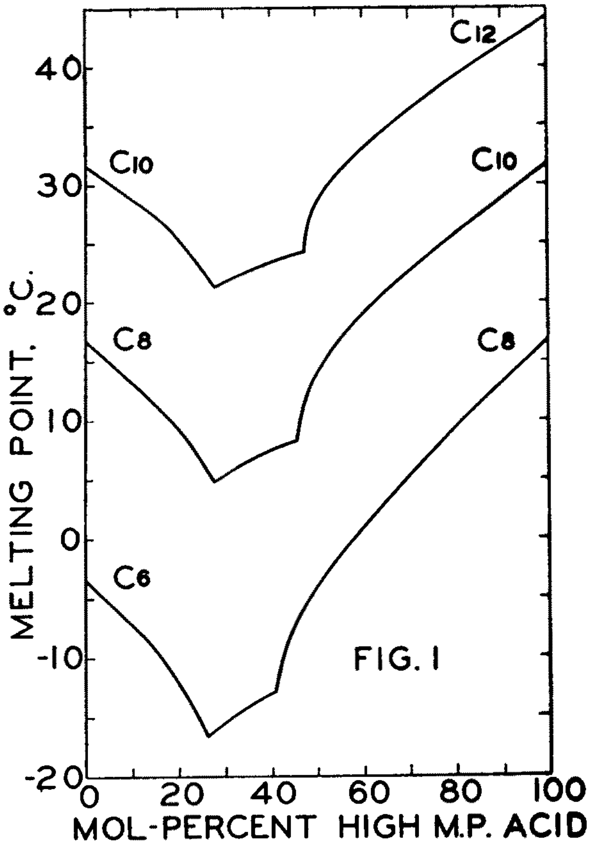

FIG. I

Application

Examples are given in Table III to demonstrate how these relations may be used in assaying purity

TABLE II

Melting Point Depression Constants

Solvent Acid	Solute Acid	Km	Kw
C_6	C_8	0.40	0.33
C_8	C_6	0.36	0.43
C_8	C_{10}	0.36	0.30
C_{10}	C_8	0.29	0.34
C_{10}	C_{12}	0.28	0.25
C_{12}	C_{10}	0.25	0.29

TABLE I

Melting Points of Binary Acid Mixtures

Caproic-Caprylic Mixture			Caprylic-Capric Mixture			Capric-Lauric Mixture		
C_8 Mol %	C_8 Weight %	M.P.°C.	C_{10} Mol %	C_{10} Weight %	M.P.°C.	C_{12} Mol %	C_{12} Weight %	M.P.°C.
0	0	−3.4	0	0	16.7	0	0	31.6
4.12	5.07	−5.1	4.20	4.97	15.2	4.36	5.02	30.4
8.30	10.10	−6.6	8.48	9.97	13.7	8.77	10.05	29.1
12.64	15.22	−8.2	12.88	15.00	12.2	13.92	15.83	27.7
16.92	20.18	−10.3	17.37	20.08	10.5	17.32	19.59	26.6
21.20	25.04	−12.8	20.64	23.71	9.0	21.81	24.49	24.5
23.51	27.62	−14.7	26.43	30.02	5.7	26.99	30.06	21.8
25.26	29.56	−15.8	27.69	31.38	5.1	28.53	31.70	21.4
28.23	32.81	−16.0	31.28	35.23	5.6	32.02	35.39	22.0
30.44	35.20	−15.4	35.43	39.60	6.5	36.03	39.58	22.7
35.22	40.30	−14.1	37.87	42.15	7.1	41.15	44.85	23.5
37.42	42.62	−13.7	44.02	48.44	8.0	45.28	49.04	24.0
40.16	45.45	−13.1	46.22	50.66	9.5	46.39	50.16	24.2
41.91	47.29	−11.2	46.78	51.22	10.7	47.76	51.53	25.5
44.18	49.56	−8.0	50.77	55.20	14.3	48.71	52.48	27.3
49.75	55.14	−4.3	56.52	60.82	17.5	50.76	54.51	29.0
55.05	60.32	−1.6	61.20	65.33	19.4	57.34	60.98	32.0
60.15	65.20	0.9	65.88	69.75	21.0	67.07	70.32	35.2
66.04	70.73	3.7	71.74	75.20	23.0	78.10	80.57	38.7
71.50	75.69	5.9	77.05	80.04	24.7	82.81	84.85	39.9
76.30	79.99	8.1	82.61	85.01	26.6	89.38	90.73	41.5
82.13	85.09	10.2	88.15	89.89	28.2	94.17	94.94	42.7
88.13	90.21	12.6	94.06	94.98	29.9	100.00	100.00	44.2
94.75	95.73	14.8	100.00	100.00	31.6			
100.00	100.00	16.7						

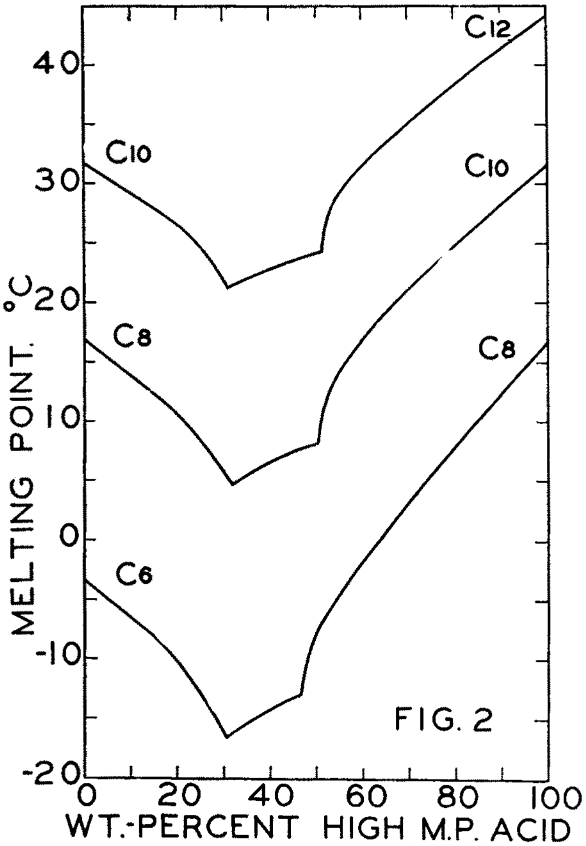

FIG. 2

of a mixture. Mixtures of pure acids were made in the proportions indicated. Their melting points were observed and molecular weight determined by titration.

In the calculations, mol per cent solute acids is obtained by dividing M.P. depression in °C. by Km, and mol per cent solvent acid by subtracting solute acids from 100. Weight per cent solvent acid is calculated by multiplying mol per cent solvent acid by the theoretical molecular weight of that acid and dividing by the molecular weight of the mixture.

TABLE III

Assay of Purity in a Mixture

Sample	1	2	3
Composition of Mixture			
Weight % C_6	0	2.95	5.78
Weight % C_8	4.01	94.01	87.71
Weight % C_{10}	91.94	3.04	6.51
Weight % C_{12}	4.05	0	0
Mol % Solvent Acid	91.74	93.81	87.42
Observed Data			
Melting Point °C	29.3	14.4	12.1
Molecular Weight	172.0	143.8	143.6
Calculated Data			
M.P. Depression °C	2.4	2.3	4.6
Km	0.285	0.36	0.36
Mol % Solute Acids	8.4	6.4	12.8
Mol % Solvent Acids	91.6	93.6	87.2
Weight % Solvent Acid	91.7	93.9	87.6
Deviation of Calculated from True Weight % Solvent Acid	−0.24	−0.11	−0.11

By the use of this method, the concentration of solvent acid may be determined with an accuracy of better than one-quarter of one per cent when present in more than 80%. For less precise work, the weight per cent solvent acid may be estimated from melting point only, using an empirical weight melting point depression constant.

Summary

The melting points of binary mixtures of adjacent even numbered carbon acids C_6 to C_{12} have been presented in table form and graphically. It has been demonstrated that by the use of the molar melting point depression constants, the purity of these acids may be readily determined to an accuracy of one-fourth of one per cent when present in a concentration of 80% or more.

The authors wish to thank Lever Brothers Company for permission to undertake and publish this work.

REFERENCES

(1) Twitchell, E., Ind. Eng. Chem., *6*, 564 (1914); *9*, 581 (1917).
(2) Wenzel, R. N., Ind. Eng. Chem., Anal. Ed. *6*, 1 (1934).
(3) Schuette, H. A., and Vogel, H. A., Oil & Soap, *16*, 209-12 (1939); *ibid.* *17*, 155-7 (1940).
(4) Hommelen, Bull, Soc. Chem. Belg., *42*, 426 (1933). Also Huntress-Mulliken, Identification of Pure Organic Compounds, Order I, page 195.
(5) Eisenstein, A., Chem. Unschau, *27*, 3 (1920).
(6) Beilstein, 4th ed., Vol. *2*, page 321.

Report of the Soybean Analysis Committee

(American Oil Chemists' Society)

During the past year, for the first time, soybeans have been sold on the basis of oil content as determined by the official A.O.C.S. method. A series of ten collaborative samples of soybeans was analyzed for oil by 79 laboratories. The results of these analyses permit an estimate of the reproducibility of these methods. Results on the first three samples may be neglected, since many laboratories had no previous experience in soybeans and the errors on these first three samples were correspondingly higher. On the last seven samples, ranging in oil content from 16.5 to 18.2 percent (14 percent moisture basis), the standard deviation in oil content ranged from 0.24 to 0.39 percent with an average of 0.34 percent. Elimination of the results of from one to six laboratories markedly improved these deviations. It was shown that the effect of the original grinding was quite important because much better agreement than the average was obtained in the case of one sample of ground soybeans submitted to the collaborators. These results compare favorably with those obtained on the 1943-1944 cottonseed check series where the average standard deviation on the first six samples is 0.31 percent.

An amplification of the present very brief official A.O.C.S. method is suggested for the benefit of laboratories using these methods for the first time. Such an amplification, based on the collaborative series, is given below. No changes are made, but the present method is given in greater detail. In view of the present successful use of these methods, any changes should be made with caution. Other types of extraction equipment and other extraction procedures may give the same results, but these should be carefully checked against the present official A.O.C.S. method before being used.

Work at the laboratories of two of the Committee