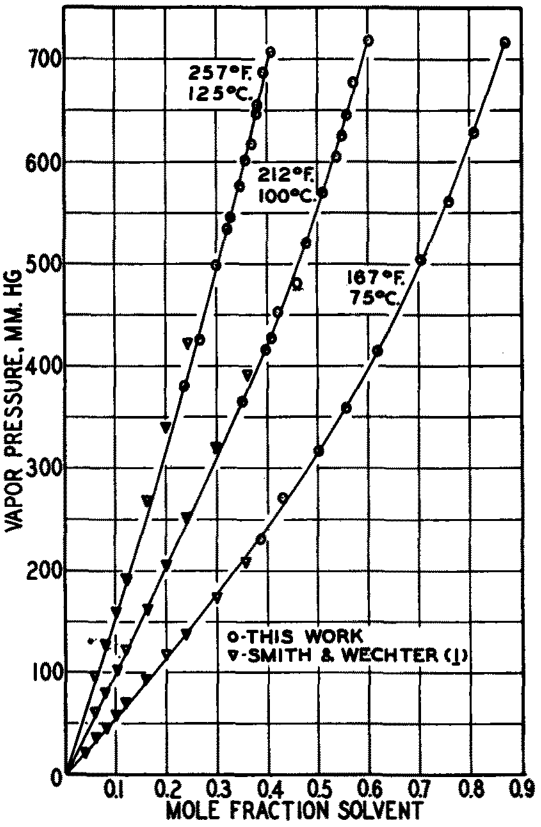

FIG. 2. Experimental vapor pressure data for soybean oil-hexane solutions.

proach to equilibrium and is in contact with the oil after that condition exists. Excess solvent distills from the flask into the condenser and is collected in a receiver cooled by ice.

After an arbitrary circulation period of two hours the solvent content of the oil was obtained by reweighing the flask. A check on the equilibrium time was made in initial runs by replacing the flask after weighing and continuing the run for various periods of time. Pressure on the apparatus was maintained by a vacuum pump operating through a regulator sensitive to ± 1 mm. A single sample of oil could be used for the measurement of several equilibrium concentrations at a constant temperature by starting at a low pressure and increasing the pressure in 50- to 100-mm. increments. The capacity of the flask limited the number of pressure-concentration values which could be obtained with one oil sample.

The crude extracted soybean oil was the same product as that used in the previous investigation. The hexane was Eastman practical grade, having a vapor pressure of 742 mm. at 153.1°F. The hexane used previously had a vapor pressure of 740 mm. at 155.3°F.

Experimental Results

The vapor pressures given in Table I are the experimental values multiplied by the ratio of the vapor pressure of the hexane used in this work to that of the hexane used in the previous work at low concentrations. The tabulated data are comparable therefore with the vapor pressures given previously for low concentrations. Justification of this method of comparing results obtained with different samples of hexane is given in a following paper. Good agreement of the two sets of data is shown by the smooth curves in Figure 2. The agreement between the data obtained by the two methods is apparently as good as that between individual results of each method. The maximum departure of experimental points from smoothed curves is about ± 2% for the concentration range covered in Table I. Interpolation of data between the experimental temperatures at high concentrations is best accomplished by plotting temperature against concentration at constant pressure.

REFERENCES

1. Smith, Allen S., and Wechter, Franklin J., J. Am. Oil Chem. Soc., *XXVII*, 381 (1950).

[*Received January 22, 1951*]

Solidification Point Curves of Binary Acid Mixtures. VII. Undecanoic to Pentacosanoic Acids[1]

H. A. SCHUETTE, R. M. CHRISTENSON,[2] UNNSTEINN H. STEFANSSON,[3] SALLIE A. FISHER,[4]
H. A. VOGEL,[2] and JOSEPH WALKER,[5] University of Wisconsin, Madison, Wisconsin

ALTHOUGH the present state of our knowledge on the occurrence of monocarboxylic *n*-acids of uneven number of carbon atoms in fatty oils probably lessens the practical interest in the solidification of point-curves of mixtures of their adjacent pairs as analytical tools, still there exists an academic interest in them if for no other reason than comparison with those of their "even" homologs.

The mixed melting point curve of binary mixtures of the C_{23} and C_{25} fatty acids which had been prepared by Chibnall and associates (1) for the purposes of reference in the identification of the acids of phrenosin and kerasin of brain tissue suggests studies which are comparable—they are not similar—to those herein reported. Even so however it could not be predicated, *a priori*, that the shape of this diagram sets the pattern for that of the solidification-point curves of binary mixtures of adjacent pairs of the lower homologs of these acids. Those of the C_8 to C_{16} group of this series are characterized by well defined inflections. These inflections are not evident however in the upper areas (4). One school of thought has described them as eutectic points at which is indi-

---

[1] Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation and in part by a grant from S. C. Johnson and Son Inc., Racine, Wis.

[2] Present address: Pittsburgh Plate Glass Co., Milwaukee, Wis.

[3] Johnson Company fellow. Present address: Reykjavik, Iceland.

[4] Present address: Rohm and Haas Company, Philadelphia, Pa.

[5] Present address: Pure Oil Co., Crystal Lake, Ill.

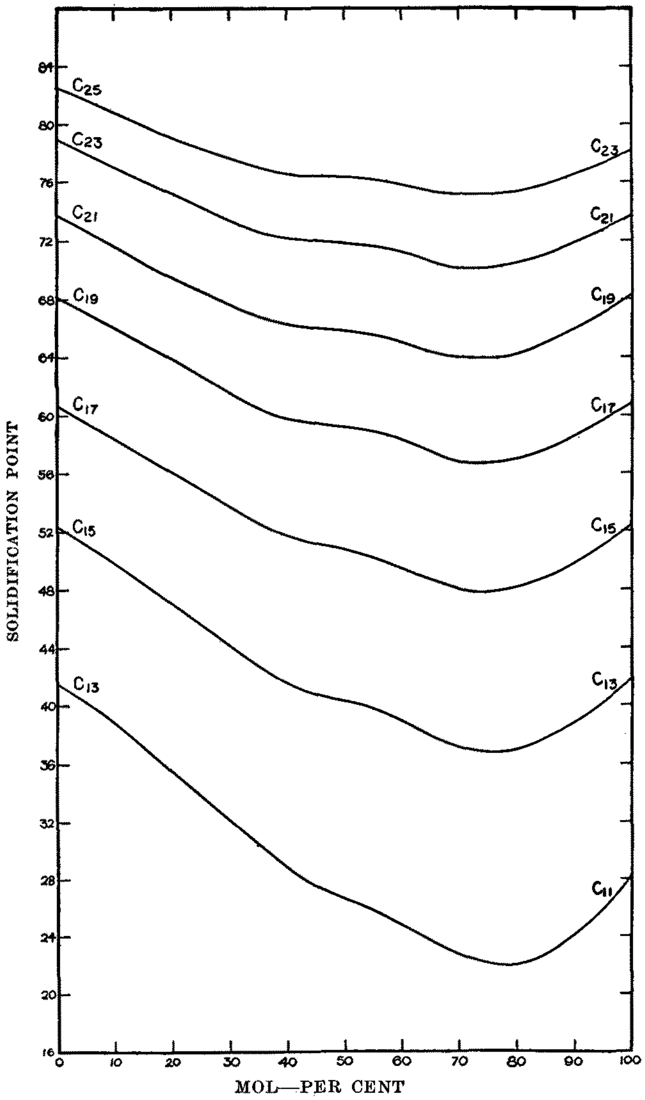

FIG. 1. Solidification point diagrams of binary mixtures of the odd acids undecanoic to pentacosanoic.

cated the formation of mixed crystals in a solid solution (6); another views them as circumstantial evidence of the formation of a compound (5) close to an equimolecular mixture of the two acids. Our observations lead us to interpret them as being the minimum solidification points of solid solution systems in which their occurs a deviation or point of inflection traceable to the tendency of the acids to associate or to form dimers.

Preparation of Materials

The acids in question were made from the next lower "even" homolog by the classical cyanide synthesis. Except as subsequently noted, the acids had originally been recovered from natural sources and were purified as described in an earlier communication (3a) in this series of reports. The point of departure in each instance was the alcohol resulting from a high pressure hydrogenation of the corresponding ethyl ester in the presence of a copper chromite catalyst.

Two different approaches were used in the preparation of arachidic and behenic acids, one serving as a check upon the other with respect to the solidification point as a criterion of purity of the product. In the first instance the stearic acid chain was progressively lengthened by means of a malonic ester synthesis; in the other the objective was reached by coupling the appropriate Grignard reagent, made from the C_{10} or C_{12} straight chain alkyl iodide, with ω-carbethoxynonyl chloride to form a 10-keto acid (3c). The keto group was subsequently catalytically reduced over Raney nickel at high pressure to the corresponding 10-hydroxy compound. Substitution of iodine for the hydroxyl group, after saponification of the ester and liberation of the acid, and subsequent treatment of the resulting iodide with zinc and acetic acid completed the synthesis. The acids were recrystallized from acetone.

Proof of the effectiveness of this method of synthesis lies in the fact that the solidification point of the respective acids agrees with that of the product obtained by malonic ester syntheses which, in turn, agrees with that previously reported. Overall yields for the method were of the order of 15 to 20 mole per cent when based on the starting acids.

TABLE I

Transition Point Data

Acid	Solidification Point		Resolidification Point[a]
Carbon Content	Observed °C. (corr.)	Reported °C.	Francis and Piper[b] °C.
11	28.20	28.2-28.4	....
13	41.76	41.0-41.6	....
15	52.40	52.0-52.4	....
17	60.84	60.8-61.17	60.85
19	68.16	68.8[b]	68.2
21	73.68	73.5[b]	73.7
23	78.11	78.69[c]	78.4
25	82.45	82.91[c]	82.7

[a] The resolidification point is that temperature at which the partly molten specimen in the capillary tube commences to resolidify when the temperature is lowered very slowly. It is a close approximation of the true solidification point.

[b] Calculated by Francis and Piper.

[c] Cited by Francis and Piper.

The solidification points (Table I) of the eight synthetic acids pertinent to this communication are in agreement with what are deemed to be the best literature values. For the C_{17} to C_{25} group the resolidification point (2), in a sense, serves as a standard of comparison, as do also the calculated values for the C_{19} and C_{21} acids submitted by Francis and Piper (2) and those cited by them for the C_{23} and C_{25} members of this series. It is not apparent however that any of the existing data on the solidification points of the uneven series of fatty acids have been obtained by the same method of procedure as that used in this laboratory.

Summary

The clearly defined inflections which characterize the solidification-point diagrams of binary mixtures of the adjacent, straight-chain acids of even number carbon atom content in the C_8 to C_{16} area of the homologous series in question are not evident when an "odd" acid enters the picture. Pertinent diagrams for the adjacent odd-odd acids, C_{11} to C_{25}, have been constructed.

Although these diagrams have probably no known analytical application at the present, they have a

---

[3] Grateful acknowledgment is made to Armour and Company, Chicago, for the gift of the "Neo Fats" as the source of the C_{10} to C_{18} acids, and to Archer-Daniels-Midland Company (The Werner G. Smith Company Div.), Cleveland, for erucic and behenic acids.

TABLE II

Solidification Points of Binary Mixtures of Fatty Acids

Undecanoic-Tridecanoic Acids		Tridecanoic-Pentadecanoic Acids		Pentadecanoic-Heptadecanoic Acids		Heptadecanoic-Nondecanoic Acids		Nondecanoic-Heneicosanoic Acids		Heneicosanoic-Tricosanoic Acids		Tricosanoic-Pentacosanoic Acids	
Composition C_{11} Acid	Solidification Point	Composition C_{13} Acid	Solidification Point	Composition C_{15} Acid	Solidification Point	Composition C_{17} Acid	Solidification Point	Composition C_{19} Acid	Solidification Point	Composition C_{21} Acid	Solidification Point	Composition C_{23} Acid	Solidification Point
mol.%	*°C.(corr.)*	*mol.%*	*°C.(corr.)*	*mol.%*	*°C.(corr.)*	*mol.%*	*°C.(corr.)*	*mol.%*	*°C.(corr.)*	*mol.%*	*°C.(corr.)*	*mol.%*	*°C.(corr.)*
0.00	41.76	0.00	52.40	0.00	60.84	0.00	68.16	0.00	73.68	0.00	78.89	0.00	82.45
8.03	39.47	16.61	48.02	7.71	59.09	15.94	64.78	7.10	72.34	10.14	77.02	7.06	81.45
16.55	36.65	27.38	44.98	16.48	57.08	31.21	61.53	13.29	71.00	15.32	76.06	12.73	80.50
24.44	34.13	37.83	41.98	23.74	55.23	37.33	60.22	16.60	70.12	20.49	75.11	17.28	79.59
31.98	31.52	43.03	41.00	32.24	53.31	39.77	59.87	26.37	68.42	26.18	74.08	24.52	78.50
38.16	29.40	45.30	40.63	37.57	52.10	42.49	59.70	34.14	67.05	31.71	73.04	28.84	77.79
43.51	27.80	48.05	40.43	42.55	51.35	45.00	59.50	40.13	66.38	36.73	72.58	35.01	77.14
46.04	27.25	50.69	40.18	45.08	51.17	47.45	59.37	47.17	66.08	41.76	72.20	40.78	76.66
48.68	26.80	53.10	39.85	47.78	50.89	52.32	59.12	53.40	65.70	46.71	71.95	46.42	76.55
53.55	26.00	58.05	39.19	52.60	50.48	57.42	58.60	59.01	65.19	52.28	71.70	52.20	76.38
58.37	25.00	62.83	38.28	57.65	49.77	62.58	58.04	64.52	64.44	56.96	71.50	57.55	76.11
63.28	23.90	67.72	37.33	62.62	49.01	67.14	57.23	71.63	64.00	62.00	71.10	65.69	75.38
68.16	22.97	70.08	37.03	67.32	48.28	72.07	56.74	76.85	63.88	66.38	70.37	71.27	75.20
72.86	22.30	72.47	36.83	72.18	47.86	74.44	56.67	83.80	64.79	71.14	70.17	75.90	75.16
75.13	22.10	74.94	36.68	74.69	47.76	76.95	56.77	88.70	65.73	76.42	70.24	83.39	75.70
77.84	21.94	77.27	36.73	76.95	47.86	81.49	57.26	94.55	66.90	81.36	70.77	88.72	76.24
82.15	22.10	81.94	37.12	81.59	48.32	87.04	58.08	100.00	68.16	86.31	71.28	90.67	76.66
87.34	23.20	91.09	39.05	87.11	49.19	93.61	59.44	......	......	90.86	72.02	97.45	77.77
93.19	25.20	95.39	40.24	93.65	50.70	100.00	60.84	......	......	94.99	72.68	100.00	78.11
100.00	28.20	100.00	41.76	100.00	52.40	......	......	......	......	100.00	73.68		

potential one in the indirect determination and characterization of the higher alcohols oxidized to the corresponding acids.

REFERENCES

1. Chibnall, A. C., *et al.*, Biochem. J., *30*, 110 (1936).
2. Francis, F., and Piper, S. H., J. Am. Chem. Soc., *61*, 577 (1939).
3. Schuette, H. A., and Vogel, H. A., Oil and Soap, (a) *16*, 209 (1939); (b) *17*, 155 (1940); (c) *22*, 238 (1945).
4. Schuette, H. A., *et al.*, *ibid.*, (a) *17*, 122 (1940); (b) *20*, 263 (1943); (c) *22*, 107 (1945); (d) *25*, 64 (1948).
5. Shriner, R. L., *et al.*, J. Am. Chem. Soc., *55*, 1494 (1933).
6. de Visser, L. E. O., Rec. trav. chim., *17*, 182 (1898).

[Received January 29, 1951]

Possibilities in Photosynthetic Methods for Production of Oils and Proteins[1]

HAROLD W. MILNER, Carnegie Institution of Washington, Department of Plant Biology, Stanford, California

THERE are innumerable ways in which green plants are useful to and necessary for the existence of man. Every bit of fuel we burn to cook our meals, to warm our homes, to drive our cars, to power our industries, all these originated from plants which grew in the past. A very great number of important industrial products are derived from plants. Every bite of food we eat can be traced directly back to plants, whether we eat the plants or plant products as such, or whether we eat an animal which, in turn, has fed on plants. The availability of an adequate food supply is of more urgent importance to the welfare of the individual man than is the production of fuel and of industrial raw materials.

Since the day, ages ago, when someone first conceived the idea of planting seeds and growing a crop, man has become increasingly dependent on farm crops for his daily food. As there were more men, there had to be more farms to feed them. The end of this sort of expansion is already in sight. There is a limit to the amount of land on earth which can be used to grow food. Some improvement, but not nearly enough, has been made in the yield of food per acre. This was mostly due to the development of new strains of plants and better methods of farming. If the world food supply is to keep pace with an increasing population, new and more efficient methods of food production must be sought.

Only the green plant can live on a strictly inorganic diet, that is, carbon dioxide, water, and a few mineral salts. Out of these it makes the organic matter without which all other living things would starve. Energy is required to convert the inorganic compounds into organic matter. A wealth of energy in the form of sunlight pours onto the surface of the earth every day. The only part of that energy which we know is converted to chemical energy and stored for future use is the light used by green plants in the process of converting carbon dioxide and water into organic matter. This process of photosynthesis upon which man depends for his very existence is grossly inefficient.

Every minute each square centimeter of the earth's surface exposed normally to the sun's rays receives 1.9 calories. A simple calculation shows that the world receives a million calories from the sun for each calorie that is available to mankind as food. There is obviously no shortage of energy for making food. Of course, much of this solar energy does not fall on green plants, and of that which does, only about half is available to the plant for use in photosynthesis. The plant can use only the wavelengths in the visible spectrum, not those in the infrared. Considering only the sunlight falling on a cultivated acre in a year, the very best crops can convert only one-half of 1% of the available solar energy into chemical energy stored as organic matter.

Most crops do not utilize nearly as much as 0.5% of the sunlight which falls on the farm because farm-

---

[1] Presented at the Fall Meeting, American Oil Chemists' Society, San Francisco, Calif., September 26, 1950.