TABLE I

MEMBRANE AND HYDROGEN ELECTRODE POTENTIALS FOR THE SYSTEM, AGARIC ACID/HYDROCHLORIC ACID

N $Ca(OH)_2$ in 50 ml. of agaric acid solution, ml.	Milliequivalents HCl in 50 ml. of agaric acid solution	Original *p*H	Final *p*H outside	Final *p*H inside	*p*H Out − *p*H In	H_2 elect. potential, mv.	Measured potential, mv.
50.0	..	3.95	4.00	3.93	0.07	4.1	3.85
25.0	..	3.64	3.73	3.64	.09	5.3	5.24
10.0	..	3.28	3.38	3.28	.10	5.9	6.00
6.0	..	3.13	3.26	3.14	.12	7.1	6.85
4.0	..	3.06	3.20	3.06	.14	8.3	8.59
3.0	..	3.02	3.19	3.03	.16	9.5	8.92
2.0	..	2.97	3.00	2.91	.09	5.3	4.82
1.0	..	2.70	2.71	2.68	.03	1.8	2.09
0.5	..	2.66	2.69	2.67	.02	1.2	1.16
..	0.0	2.48	2.48	2.47	.01	0.6	0.92
..	0.5	1.79	1.80	1.78	.02	1.2	.88
..	1.0	1.42	1.47	1.41	.06	3.6	1.19
..	2.0	1.20	1.23	1.20	.03	1.8	1.59
..	3.0	1.09	1.10	1.04	.06	3.6	2.85
..	4.0	1.01	1.02	0.94	.08	4.7	4.85
..	5.0	0.98	0.99	.91	.08	4.7	4.15
..	6.0	.94	.95	.90	.05	3.0	2.99
..	10.0	.72	.73	.71	.02	1.2	1.05
..	12.0	.71	.72	.70	.02	1.2	1.07

is shown in Table I where the observed P. D. (Measured Potential) is found to be in reasonably good agreement with the hydrogen electrode potential calculated from the *p*H values of the two solutions (measured at the end of the experiment). The membrane potential thus obtained arises from the unequal distribution of H^+ and Cl^- on opposite sides of the membrane. Tests of the hydrogen chloride solution revealed that neither Ca^{++} nor agarate ions passed through the membrane in detectable quantities.

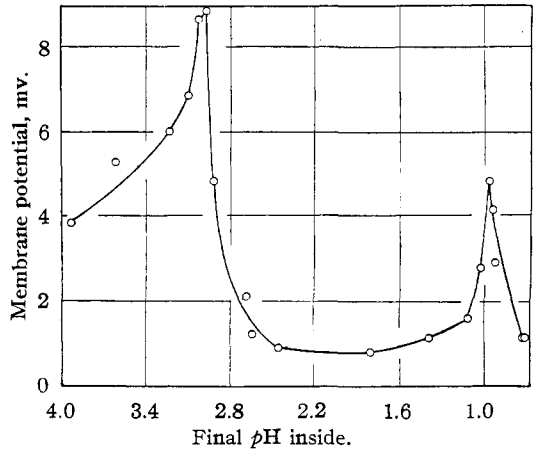

Fig. 1.—Relationship between *p*H and membrane potential.

When the final *p*H inside is plotted against the measured membrane potential, two maxima are found at *p*H values of approximately 3.0 and 1.0 (see Fig. 1). The second maximum is attributed to the hydrolytic decomposition of the agar. Since the membrane potential of such systems is a colligative property depending upon the number of discrete discontinuities of the dissolved constituent present, it is to be expected that the membrane potential will vary as a function of the concentration of the osmotically active particles. Agaric acid, a polyuronide, yields uronic acid units and reducing sugars.[4] Therefore, a second equilibrium is to be expected at *p*H values of approximately 1.0 where the agar complex is known to hydrolyze into simpler units.

(4) A. G. Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Oxford University Press, Oxford, England, 1937.

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Melting Points of the *p*-Bromoanilides of Solid Fatty Acids[1]

BY DAVID F. HOUSTON

The melting points of the *p*-bromoanilides of certain solid fatty acids recently prepared in this Laboratory differ greatly from those in the literature.[1a] Several of our results agree with those previously ascribed to higher homologs. A graph of our values has the general form of the melting-point curves of aliphatic series; that of

(1) Not subject to copyright.

(1a) P. W. Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).

TABLE I

ANALYSES AND MELTING POINTS OF THE *p*-BROMOANILIDES OF SOLID FATTY ACIDS

p-Bromoanilide	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Bromine Calcd.	Bromine Found	Melting point in °C. Lit.[c]	Melting point in °C. Found
Capric	58.92	59.03[a]	7.37	7.54[a]	24.6	24.7[b]	102	101.9
Lauric	61.02	61.02	7.94	7.93	22.6	22.5	104	106.7
Myristic	62.81	62.94	8.41	8.26	20.9	21.2	107	110.2
Palmitic	64.38	64.33	8.81	8.74	19.5	19.2	110(114)[d]	113.2
Stearic	65.72	65.63[a]	9.16	9.38[a]	18.3	18.4[b]	114	115.2

[a] Analyses by W. T. Haskins, National Institute of Health; all others by C. J. Rodden, National Bureau of Standards. [b] Pregl method. Other bromine analyses by Zacherl and Krainick method. [c] Robertson's values[1a] except *d*. [d] Acree and LaForge (*J. Org. Chem.*, **2**, 308 (1937)). A sample of their material showed a melting point of 113.1° when determined by the writer by means of the Francis and Collins method.

the literature values has an opposite convexity. Hence it has seemed wise to publish our results.

The reagent quality acids were first recrystallized from concentrated sulfuric acid[2] until no further discoloration of the solvent occurred, and they were then repeatedly recrystallized interchangeably from acetone, benzene, and glacial acetic acid until no further change in melting point occurred. The acids were converted into their acid chlorides with thionyl chloride.

The *p*-bromoaniline was prepared (a) by the reduction of *p*-nitrobromobenzene (m. p. 126.3°), (b) by hydrolysis of *p*-bromoacetanilide (m. p. 168.6°) according to Vecchiotti,[3] and (c) by recrystallization of a commercial product from chloroform and then from aqueous alcohol to remove colored matter[4] and tribromoaniline, respectively. The three preparations of *p*-bromoaniline thus obtained had melting points between 63.5 and 64.0°, and gave products with palmitic acid which had identical melting points.

The chlorides were treated with a benzene solution of *p*-bromoaniline according to the procedure of Kuehn and McElvain,[5] with the single modification of first crystallizing the product directly from the benzene solution instead of evaporating the benzene. In the case of the long chain acids, this affords a more rapid purification.

The melting points were determined with a partial-immersion thermometer (calibrated at this Bureau) by the improved capillary-tube method of Francis and Collins.[6] This procedure, which maintains an extremely slow rate of temperature rise at the melting point, gives values that are somewhat lower than those usually obtained by capillary-tube methods (see footnote *d* of table). The results are, however, in better agreement with those obtained by equilibrium measurements on larger amounts of material.

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(2) F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. London*, **A158**, 706 (1937).

(3) L. Vecchiotti, *Gazz. chim. ital.*, **58**, 231 (1928).

(4) W. M. D. Bryant, THIS JOURNAL, **60**, 2748 (1938).

(5) M. Kuehn and S. M. McElvain, *ibid.*, **53**, 1173 (1931).

(6) F. Francis and F. J. E. Collins, *J. Chem. Soc.*, 137 (1936).

The Separation of Hydroxy from Non-hydroxy Fat Acids by Means of a Dibasic Acid Anhydride[1]

BY FLOYD E. KURTZ[2] AND P. S. SCHAFFER[2]

The methods used for separating hydroxy from non-hydroxy fat acids have been based for the most part on differences in physical properties of the acids or of the derivatives formed with the carboxyl group. When the fat acid mixture contains acids in which these differences are small, it becomes difficult to secure a separation by such methods. This is particularly true if one of the similar acids is present as a minor constituent while the other is present in a high concentration.

In the method proposed here, the mixed esters are heated with a dibasic acid anhydride, the reaction mixture is dissolved in petroleum ether, and the derivative formed with the hydroxy esters is extracted with alkali. Since this method consists in the separation of an alcoholic from a non-alcoholic compound rather than upon the separation of two acids, its efficiency is not affected by a similarity in the physical properties of the acids.

Of the most readily available dibasic acid anhydrides, phthalic anhydride was considered unsuitable because of the difficulty of freeing the recovered fat acids from phthalic acid. Maleic anhydride was thoroughly investigated. It formed derivatives with methyl ricinoleate and with 12-hydroxymethylstearate which could be extracted readily from petroleum ether solutions, less readily from ether solutions, by means of dilute potassium hydroxide. Since ricinoleic acid and 12-hydroxystearic acid represent two hydroxy acids with quite different physical properties, it is considered likely that similar results could be ob-

(1) The part relating to maleic anhydride was presented before the Division of Biological Chemistry at the 97th meeting of the American Chemical Society, April 3–7, 1939, at Baltimore, Maryland. (Not subject to copyright.)

(2) Division of Dairy Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.