Further data, with reference to types of compounds which undergo reduction as well as replacement of active hydrogen, are presented in Tables I-III. The agreement with the theory is in general within the limits of experimental error.

It was occasionally desirable to run larger scale reactions in order that reaction products might be investigated. Some of these are described in Table IV, the procedures having been described previously.[4]

Experimental

Early experiments were carried out with the usual type of micro-scale Grignard machine,[10] the reactions being performed in air. Erratic results, due to a slow reaction of the hydride with oxygen and the consequent liberation of hydrogen, were remedied by carrying out the operations in an atmosphere of nitrogen. Difficulties encountered because of the leaking and fouling of the three-way stopcock were overcome by a modification of the apparatus. Dioxane, anethole and N-methylmorpholine are less satisfactory than dibutyl ether as a solvent, while N-ethylmorpholine is the most satisfactory solvent used to date. Pyridine cannot be used since it is reduced by the reagent.

The design of the apparatus is shown in Fig. 1. It may be noted that if an accuracy of better than one per cent. is desired, the design should be altered to minimize the free space in the head of the reaction vessel and in the connections to the gas buret, and also that the latter should be maintained at constant temperature.

The operation of the apparatus is similar in principle to that described by Soltys.[10] A weighed sample is placed in the reaction vessel, L, the apparatus is flushed with dry nitrogen, and the desired quantity of solvent is added from the buret, D. The gas buret is levelled at zero, and with stirring by the magnetic bar, M, the desired quantity of lithium aluminum hydride solution (taken in 20-30% excess) is added from buret, B. The evolution of hydrogen from compounds containing active hydrogen is usually complete in one to ten minutes at room temperature; reduction reactions may require a longer time, or may require heating. After measurement of the hydrogen gas volume, the excess hydride is decomposed by the addition, from buret, C, of 1.0 ml. of a mixture of amyl alcohol in two volumes of dibutyl ether. Complete decomposition of the reagent may require some time; usually fifteen minutes at room temperature is adequate.

Reagents.—Stock solutions of lithium aluminum hydride were prepared by shaking 2 g. of the compound[11] with 200 ml. of dibutyl ether for fifteen minutes or longer, allowing the mixture to settle and filtering the supernatant liquid through sintered glass, all operations being conducted under nitrogen. This yields a clear solution, 0.20-0.25 molar in $LiAlH_4$, which slowly deposits a white precipitate and deteriorates at a rate of less than 1% per month when stored under dry nitrogen.

The solvents, N-ethylmorpholine and dibutyl ether, were first dried over calcium hydride, then treated with lithium aluminum hydride (2 g. per l.) at 90-100° for two hours, and were then distilled at 20 mm. pressure. After placing the solvent in the reservoir, control runs were made on the basis of which the calculated quantity of lithium aluminum hydride solution was added to the solvent contained in the reservoir and the mixture heated to 70° for one hour. With this procedure the quantity of hydrogen liberated from 1 ml. of solvent by the addition of hydride solution could be made smaller than 0.05 ml.

Cylinder nitrogen was used without purification, other than drying over phosphorus pentoxide.

The test compounds were purified by conventional procedures but with special care to exclude moisture. In the recrystallization of solids it was necessary to avoid the use of hydroxylic solvents. Liquids were dried over calcium hydride where possible, otherwise over Drierite.

Acknowledgments.—Dr. Weldon G. Brown offered much helpful advice in the development of this method; he supplied many of the compounds tested in the apparatus.

Summary

The quantitative aspect of the reaction of lithium aluminum hydride with several types of organic compounds has been investigated. It is shown that lithium aluminum hydride may be used as a reagent for the determination of active hydrogen, and reducible groups.

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[10] Soltys, *Mikrochemie*, **20**, 107 (1937). See also Niederl and Niederl, "Micromethods of Quantitative Organic Elementary Analysis," J. Wiley and Sons, Inc., New York, N. Y., 1938, p. 206.

[11] Lithium aluminium hydride was prepared in this Laboratory by the method of Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

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An Empirical Expression for the Melting Points of the Straight-Chain Dicarboxylic Acids

BY JOHN G. ERICKSON

It was pointed out by Baeyer[1] in 1877 that the melting points of the unsubstituted aliphatic dibasic acids are of an oscillatory nature, that is, the melting points of successive members of the series are alternately high and low. The melting points converge to an asymptotic value, the melting points of the acids with an even number of carbon atoms decreasing and the melting points of the acids with an odd number of carbon atoms increasing with the length of the carbon chain. The convergence value for the dibasic acids is 123°. This oscillation is not peculiar to the melting points of the dicarboxylic acids; other homologous series, including aliphatic monobasic acids and their α-hydroxy derivatives, α,α'-dibromodicarboxylic acids, dinitriles, glycols, diamines, dialdehydes, alcohols and paraffins, show similar oscillatory effects and other physical properties, including solubilities, molecular volumes, optical rotatory powers and dissociation constants are affected. However, the oscillatory or "alternating" effect is much the most pronounced with the dicarboxylic acids and has attracted the most atten-

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[1] Baeyer, *Ber.*, **10**, 1286 (1877).

tion with these compounds. The effect has been discussed by a number of persons[2] and explanations have been offered. A good summary of the conclusions reached is given by Ralston.[3]

King and Garner[4] have fitted a mathematical expression to the melting points of the ethyl esters of the saturated straight-chain monocarboxylic acids. This is a series which shows a slight alternating effect in the sense that, while the melting points for both even and odd numbered esters increase with the length of the carbon chain, the differences between successive members of the series are alternately relatively large and small. These differences become small as the chain becomes long so that, plotted as melting point *vs.* length of chain, the even and odd numbered esters give two curves which rise and tend to converge as the carbon chain increases in length. King and Garner found that the melting points could be represented by the following equation: for esters of even acids

$$T_m = \frac{0.7630n + 0.63}{0.00179n + 0.01475},\ \text{up to } n = 20$$

and

$$T_m = \frac{0.7081n - 3.28}{0.001796n - 0.0012}\ \text{above } n = 20$$

for esters of odd acids

$$T_m = \frac{0.8389n - 5.58}{0.00224n - 0.00904}$$

T_m represents the melting points and n, the number of carbon atoms in the acid.

This paper reports an expression which shows the alternating effect and convergence for the dicarboxylic acids and reproduces their melting points, from glutaric acid on, with a fair degree of accuracy. It is of a type quite different from that of King and Garner and takes the form of a single sequence, applicable over the entire range of values. It may be expressed:

$$\begin{aligned}(T_m)_n &= ab^{cd_{n-1}} + e = ad_n + e\\ (T_m)_{n+1} &= ab^{cd_n} + e = ad_{n+1} + e\\ (T_m)_{n+2} &= ab^{cd_{n+1}} + e = ad_{n+2} + e,\ \text{etc.}\end{aligned}$$

where $(T_m)_n$ represents the melting point of a dibasic acid, $(CH_2)_n(COOH)_2$, where n is greater than two, and a, b, c and e are constants whose values are: $a = 100.00$, $b = 0.09500$, $c = 0.85000$, $e = 80.000$. Each term in the d_n sequence, $d_n = b^{cd_{n-1}}$, $d_{n+1} = b^{cd_n}$, $d_{n+2} = b^{cd_{n+1}}$, etc., is calculated from the preceding one. The initial term for this sequence is $d_2 = 0.87300$.

The results are summarized in Table I, where calculated and reported values are given. The reported values were taken from Beilstein, fourth edition, Vol. II and its first and second supplements except where otherwise noted. The reported values which fit the calculated values best are given first, followed by other reported values in parentheses. The experimental values to which this expression was fitted were, with two exceptions (C_{11} and C_{21} acids), the highest values reported for each acid since it was felt, in the absence of other generally applicable criteria, that

TABLE I

MELTING POINTS OF THE DIBASIC ACID, $(CH_2)_n(COOH)_2$

n	d_n	T_m (calcd.)	T_m (observed)	
3	0.17435	97.4	97.5	(97, 97–98, 98, 98–99)
4	.70550	150.6	150.6	(149–149.5, 150, 151, 152, 153, 153–153.5)
5	.24376	104.4	105	(103, 105–106, 105–105.5)
6	.61401	141.4	141	(140, 144)
7	.29273	109.3	109	(106, 106.2, 106.5, 107, 107.5, 107–108)
8	.55672	135.7	134.5	(130–132,[a] 133–133.5)
9	.32828	112.8	111	(100–101, 109, 110, 124)
10	.51849	131.8	129	(123, 124, 124–125, 124.5–125.5, 125.5–127, 126.5–127, 127, 127–128,[b] 127.8–128)
11	.35438	115.4	114	(112, 112–113, 113, 113.5)
12	.49212	129.2	126.5	(123, 124, 125.8)
13	.37358	117.4	114.6–114.8	(111,[c] 113, 113–114)
14	.47356	127.4	125	(123, 123–124, 124, 124–124.2)
15	.38770	118.7	118	(116–117)
16	.46938	126.0	124.6–124.8[d]	(118, 124, 124.2–124.6[e])
17	.39807	119.8	119–120.5	(119.2)
18	.45092	125.1	124–125[f]	(123,[c] 123.8–124.2,[e] 125.7–125.9[g])
19	.40568	120.6	118–120	(117–117.5, 117.7–117.9, 123[c])
20	.44411	124.4	123.5–124.5[h]	(120–122,[i] 121, 123.75, 123–124, 124,[j] 122.5–124.5,[k] 125.7–126.3,[l] 126.9–127.1,[g] 123)
21	.41221	121.2	127.5[m]	
22	.43834	123.8	126.9–127.1[g]	(128–130[n])
23	.41601	121.6		
24	.43502	123.5	123.5	
25	.41878	121.9		
26	.43262	123.3		
27	.42080	122.1		
28	.43087	123.1	123.25	
29	.42228	122.2		
30	.42960	123.0		
31	.42311	122.3		
32	.42889	122.9	123	

[a] Korshak and Rafikov, *C. A.*, **39**, 4592 (1945). [b] Walker, *J. Chem. Soc.*, 1304 (1940). [c] Chuit and Hauser, *Helv. Chim. Acta*, 12, 850 (1929). [d] Ruzicka, Plattner and Widmer, *Helv. Chim. Acta*, **25**, 1086 (1942). [e] Siina, *C. A.* **32**, 499 (1938). [f] Ruzicka, Plattner and Widmer, *Helv. Chim. Acta*, **25**, 604 (1942). [g] Siina, *C. A.* **33**, 7278 (1939). [h] Zetsche and Bähler, *Helv. Chim. Acta*, 14, 632 (1931). [i] Ross, Gebhart and Gerecht, THIS JOURNAL, **67**, 1275 (1945). [j] Zetsche and Bähler, *Helv. Chim. Acta*, 14, 846 (1931). [k] Drake, Carhart and Mozingo, THIS JOURNAL, **63**, 617 (1941). [l] Siina, *C. A.* **34**, 7638 (1940). [m] Flaschenträger and Halle, *Z. physiol. Chem.*, **190**, 120 (1930). [n] Ruzicka and Stoll, *Helv. Chim. Acta*, **16**, 493 (1933).

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(2) (a) Biach, *Z. physik. Chem.*, **50**, 61 (1905); (b) Falk and Nelson, THIS JOURNAL, **32**, 1637 (1910), and *J. prakt. Chem.*, **88**, 101 (1913); (c) Pauly, *Ann.*, **383**, 260 (1911), and *Z. anorg. Chem.*, **119**, 271 (1921); (d) Tammann, *ibid.*, **109**, 221 (1920), and **115**, 288 (1921); (e) Stark, *ibid.*, **719**, 292 (1921); (f) Meerwein, *Ann.*, **419**, 121 (1921); (g) Cuy, *Z. anorg. Chem.*, **115**, 273 (1921); (h) Fairweather, *Phil. Mag.*, [7] **1**, 944 (1926); (i) Normand, Ross and Henderson. *J. Chem. Soc.*, 2632 (1926); (j) Nekrassow, *Z. physik. Chem.*, **128**, 203 (1927); (k) Malkin, *Nature*, **127**, 126 (1931); (l) King and Garner, *J. Chem. Soc.*, 1368 (1936).

(3) Ralston, "Fatty Acids and their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 324 and 353.

(4) King and Garner, *J. Chem. Soc.*, 1449 (1934); ref. 21.

the highest melting points would correspond to compounds of the greatest purity. In view of this, it is not surprising that most of the values which agree most closely with the calculated values are also the highest reported values. It will be seen that, in general, the difference between the calculated and observed values for an acid is considerably less than the range of values reported for the acid. The large difference, 6.3°, between calculated and observed melting points for the C_{23} acid may be attributed to the fact that this acid was isolated from a naturally occurring wax and the difficulties of purifying long-chain compounds when contaminated with compounds of nearly the same properties are rather great. The melting points for the C_{26}, C_{30} and C_{34} acids were taken from the very careful work of Fairweather[2h] and definitely fix the convergence value of the series as 123°.

Summary

An empirical expression, which takes the form of a mathematical sequence is proposed for the melting points of the unsubstituted dicarboxylic acids. It is shown that this expression reproduces the melting points of these acids satisfactorily.

RESEARCH DIVISION
AMERICAN CYANAMID CO.
STAMFORD, CONN.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXVII. The Conductance of Some Long Chain Salts in Acetone–Water Mixtures[1]

BY HOWARD S. YOUNG,[2] PHILIP F. GRIEGER[3] AND CHARLES A. KRAUS

I. Introduction

The effect of added methanol on the conductance of several long chain electrolytes (principally *n*-octadecyltrimethylammonium salts) in aqueous solution has been described in preceding numbers of this series.[4,5,6]

Based on the form of their conductance curves in water and mixtures of water with other solvents, long chain salts may be divided into three classes: I, the conductance curve exhibits a breakpoint in water as well as in mixtures of water with other solvents; II, the curve exhibits a maximum in water as well as in its mixtures; and III (an intermediate case), the curve exhibits a breakpoint in water and a maximum in mixtures containing sufficient additive.

Solutions of the octadecyltrimethylammonium ion have been measured in combination with seven different gegenions in methanol–water mixtures. Of these, the bromide, nitrate and oxalate fall into Class I; the chloride, bromate, iodate and formate fall into Class III. Of the octadecylpyridonium salts measured, the bromide and nitrate fall into Class I, the chloride falls into Class III and the iodate into Class II.

In the present investigation, the conductance of three octadecyltrimethylammonium salts (oxalate, formate and bromate) was measured in acetone–water mixtures (0 to 30% acetone by weight) in order to compare the effects of added acetone with those observed with methanol. Although the measurements with acetone are less extensive than those with methanol,[3,4] they permit of an adequate comparison in the case of several salts.

Among other things, it was of interest to determine whether salts in acetone–water mixtures fall into the methanol–water classification groups. It was also of much interest to determine whether or not the critical phenomenon (breakpoint or maximum) may be correlated with the physical constants of the solvent mixtures, such as dielectric constant.

II. Experimental

Apparatus and Procedure.—The details appertaining to these have been fully described in earlier numbers of this series.[4] All measurements were made at 25 ± 0.01°.

Salts.—The salts were identically the same as those used in a previous investigation.[5]

Solvents.—Water was prepared according to the technique already described[4]; its specific conductance was in the neighborhood of 1×10^{-6}.

Acetone.—Commercial acetone was treated by the silver hydroxide method described by Werner.[7] The water introduced in this treatment was removed by refluxing over anhydrous potassium carbonate. The carbonate was removed by filtration, and the acetone was fractionally distilled from activated alumina. It was freshly distilled from activated alumina immediately before use. The lowest specific conductance obtained in this manner was 6×10^{-9}.

III. Results

In Tables I, II and III are recorded selected values of the equivalent conductance, Λ, as a func-

[1] This paper is based on a portion of a thesis presented by Howard S. Young in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1948.

[2] University Fellow, Brown University, 1947–48. Present address: Tennessee Eastman Corporation, Kingsport, Tenn.

[3] Lalor Foundation Fellow, Brown University, 1947–48. Present address: Department of Chemistry, The University of Illinois, Urbana, Illinois.

[4] Evers and Kraus, THIS JOURNAL, **70**, 3049 (1948).

[5] Grieger and Kraus, *ibid.*, **70**, 3803 (1948).

[6] Brown, Grieger and Kraus, *ibid.*, **71**, 95 (1949).

[7] Werner, *Analyst*, **58**, 335 (1933).