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.

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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-

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[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.

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[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).

TABLE I

CONDUCTANCE OF *n*-OCTADECYLTRIMETHYLAMMONIUM OXALATE IN WATER–ACETONE MIXTURES AT 25°

$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ
Water $\kappa_0 = 0.89 \times 10^{-6}$, $d = 0.9971$, $D = 78.48$		13.89% Acetone $\kappa_0 = 0.76 \times 10^{-6}$, $d = 0.9783$, $D = 71.0$		9.91% Acetone $\kappa_0 = 0.84 \times 10^{-6}$, $d = 0.9834$, $D = 73.2$		20.69% Acetone $\kappa_0 = 0.56 \times 10^{-6}$, $d = 0.9685$, $D = 67.2$		28.84% Acetone $\kappa_0 = 0.98 \times 10^{-6}$, $d = 0.9564$, $D = 62.6$	
0.779	88.60 (14)	1.101	68.33 (8)	0.808	71.90 (15)	1.177	61.78 (6)	1.177	57.40 (11.0)
0.935	82.75	1.234	68.73	1.039	72.80	1.327	61.73	1.391	56.68
1.086	65.50	1.433	68.29	1.181	73.04	1.542	61.58	1.655	56.15
1.328	48.32	1.781	60.15	1.439	62.46	2.010	61.30	2.166	55.45
1.503	40.33	2.059	48.97 (4)	1.620	52.59	2.237	61.14 (2)	2.373	55.24 (3)
1.803	31.63	2.531	37.20	1.899	42.22	2.570	59.54	2.661	55.13
2.284	24.55	2.929	31.04	2.134	35.93	2.884	54.02	3.237	54.63
3.536	17.12 (4)	3.521	25.27	2.499	29.77 (5)	3.360	44.74	3.734	53.79
5.037	13.82	4.012	22.18	2.790	26.34	3.767	38.47 (1)	4.196	52.82 (1)
5.632	13.11	4.870	18.71 (2)	3.216	22.85	4.378	31.95	4.831	50.14
6.588	12.23	6.805	15.02	3.601	20.62	4.910	27.89	5.778	43.01
8.479	11.19 (1)	8.190	13.68	4.165	18.39	5.718	23.62	6.562	37.45
		10.71	12.40 (0.5)	4.677	16.93 (2)	6.529	20.75	7.884	30.59 (0.5)
				5.428	15.45	7.796	17.81 (0.5)	10.69	22.60
				6.277	14.28	10.06	15.01		
				7.674	13.08				
				10.70	11.78 (0.6)				

TABLE II

CONDUCTANCE OF *n*-OCTADECYLTRIMETHYLAMMONIUM FORMATE IN WATER–ACETONE MIXTURES AT 25°

$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ
10.00% Acetone $\kappa_0 = 0.97 \times 10^{-6}$ $d = 0.9833$, $D = 73.1$		13.89% Acetone $\kappa_0 = 0.76 \times 10^{-6}$, $d = 0.9783$, $D = 71.0$	
1.303	57.69 (9.0)	1.390	55.52 (7)
1.490	58.22	1.543	55.59
1.847	59.23	1.738	55.73
2.171	62.68	1.913	56.02
2.635	66.78	2.134	56.71 (3)
3.087	68.22	2.325	57.83
3.881	66.62	2.580	59.49
4.551	63.65	2.906	61.15
5.666	57.92 (0.5)	3.441	62.76 (1)
6.668	54.12	3.952	62.87
8.134	49.09	4.702	61.51
11.57	41.71 (0.2)	5.215	59.99
		6.003	57.56
		8.074	51.22 (0.2)

TABLE III

CONDUCTANCE OF *n*-OCTADECYLTRIMETHYLAMMONIUM BROMATE IN 10.00% ACETONE AT 25°

$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ
$\kappa_0 = 0.97 \times 10^{-6}$, $d = 0.9833$, $D = 73.1$		$\kappa_0 = 0.97 \times 10^{-6}$, $d = 0.9833$, $D = 73.1$	
1.280	60.71 (9)	3.028	66.87
1.480	60.91	3.703	62.70
1.663	61.28	4.245	58.42 (1)
1.821	61.85	5.152	51.58
2.023	63.71	6.015	46.34
2.331	66.31	7.404	40.18
2.609	67.83 (2)	10.33	32.88 (0.3)

tion of the square root of equivalent concentration, C, for *n*-octadecyltrimethylammonium oxalate, formate and bromate, respectively. The numbers in parentheses in the tables are the percentage solvent correction; they are included to indicate the magnitude of this correction. The solvent composition is given in weight per cent. The following data are included for the solvents: specific conductance, κ; density, d[8]; and dielectric constant, D.[9] In computing the equivalent concentration, the densities of the solutions were assumed equal to those of the pure solvents[3]; no buoyancy corrections were applied.

In Figure 1, Λ is plotted against $\sqrt{C}$ for *n*-octadecyltrimethylammonium oxalate in acetone–water mixtures. Earlier results[4] with water as solvent are included in the figure for comparison. In Figs. 2 and 3 are shown similar plots for the formate and the bromate. Previous results[4,10] with water and water–methanol mixtures as solvents are also plotted for purposes of comparison.

IV. Discussion

As may be seen from an inspection of Figs. 1, 2 and 3, the effect of added acetone on the conductance of octadecyltrimethylammonium salts in water is similar to that of methanol. In methanol–water mixtures, the oxalate shows the simple breakpoint phenomenon (Class I); an analogous situation prevails in acetone–water mixtures. Similarly, the bromate and formate, which exhibit a maximum in Λ in methanol–water mixtures (Class III), likewise exhibit a maximum in acetone–water mixtures.

The low value of the breakpoint concentration of octadecyltrimethylammonium oxalate in water and the wide range of concentration over which it is displaced on addition of added solvents render this salt particularly useful in any attempt to correlate the breakpoint concentration with the

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[8] Determined with a Weld type specific gravity bottle. Good agreement was found with the results of McElroy, THIS JOURNAL, **16**, 618 (1894).

[9] Albright, *ibid.*, **59**, 2098 (1937).

[10] Carignan, Thesis, Brown University, 1947.

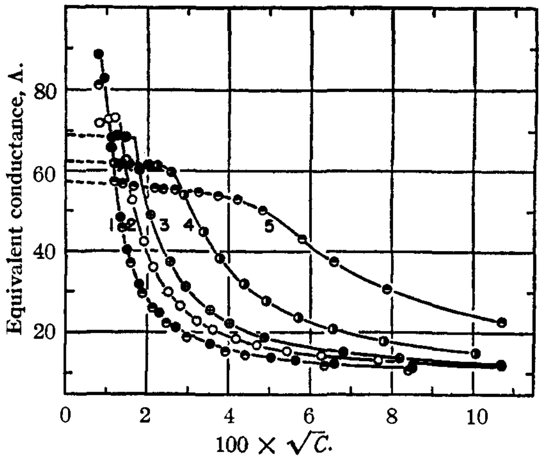

Fig. 1.—Octadecyltrimethylammonium oxalate in: water (1); acetone: (2) 9.9%; (3) 13.9%; (4) 20.7%; (5) 28.8%.

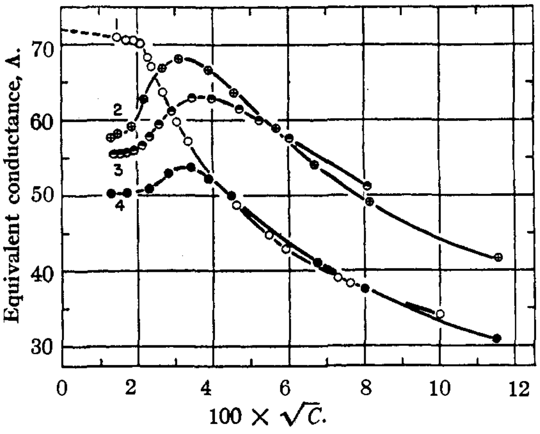

Fig. 2.—Octadecyltrimethylammonium formate in: water (1); acetone: (2) 10.0%; (3) 13.9%; methanol: (4) 19.4%.

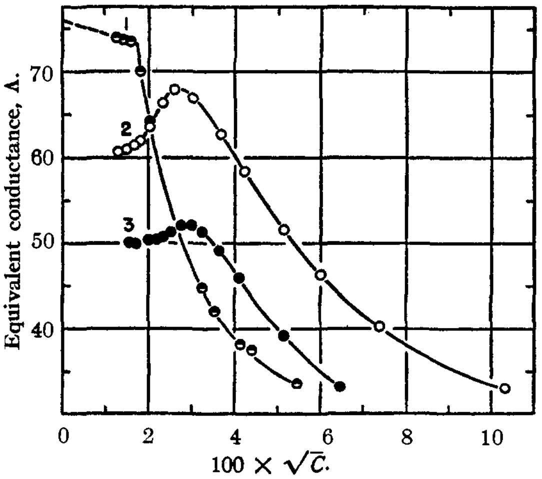

Fig. 3.—Octadecyltrimethylammonium bromate in: water (1); acetone (2) 10.0%; methanol (3) 20.7%.

physical properties of the solvent mixtures. For smaller additions of acetone or methanol, the breakpoint remains quite sharp, but, for larger additions, for example, 28.8% acetone, the breakpoint concentration can only be approximated.

Breakpoint concentrations for octadecyltrimethylammonium oxalate in acetone–water and methanol–water mixtures are given in Table IV.[11] The composition of the solvent is given in terms of both weight per cent. and mole per cent. of additive. The reciprocal of the dielectric constant of the solvent (column 3) and the logarithm of the breakpoint concentration (column 5) are also given.

TABLE IV

BREAKPOINT CONCENTRATION, C_b, OF *n*-OCTADECYLTRIMETHYLAMMONIUM OXALATE IN ACETONE–WATER AND METHANOL–WATER MIXTURES

Wt. % org. comp.	Mole % org. comp.	$10^2/D$	$10^2\sqrt{C_b}$	$4 + \log C_b$
		Acetone		
0	0	1.274	0.8	−0.19
9.91	3.30	1.366	1.2	+0.158
13.9	4.76	1.408	1.6	.408
20.7	7.48	1.488	2.3	.724
28.8	11.1	1.597	3.6	1.123
		Methanol		
20.7	12.7	1.435	1.64	0.428
30.2	19.5	1.529	2.6	.828
40.1	27.3	1.642	4.2	1.246

Inspection of Table IV will show that on a weight per cent. basis, acetone increases the breakpoint concentration more than does methanol. The relationship is shown clearly in Fig. 4

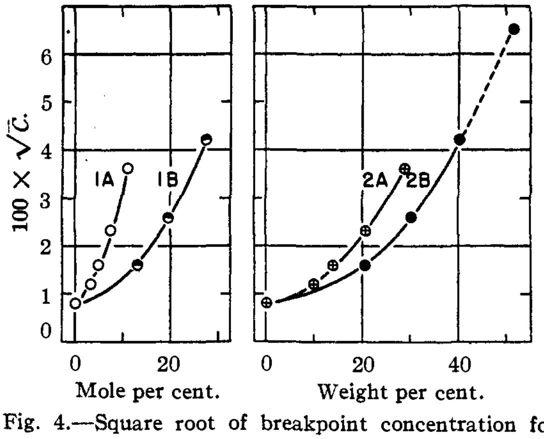

Fig. 4.—Square root of breakpoint concentration for octadecyltrimethylammonium oxalate as function of composition for: water–acetone mixtures (A); water–methanol mixtures (B); Composition: mole per cent, curves 1; weight per cent, curves 2.

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[11] The breakpoint concentration of the oxalate in water has not been evaluated experimentally. However, according to Dakin, THIS JOURNAL, 63, 1007 (1941), the conductance of the oxalate ion is known to be 74.1 and that of the octadecyltrimethylammonium ion[4] 18.3, yielding a value of approximately 92 for the equivalent conductance of the oxalate. If a line be drawn from the Λ axis from the point corresponding to this value and according to the theoretical slope, its intersection with the extension of the experimental curve at higher concentration should give an approximate value of the breakpoint. This procedure leads to the value $\sqrt{C} = 0.8 \times 10^{-2}$.

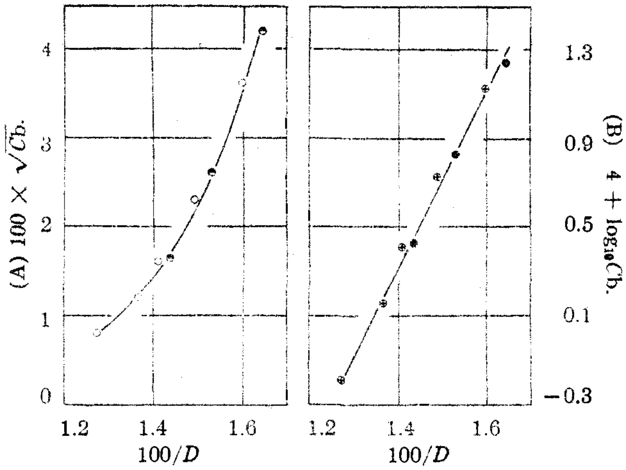

Fig. 5.—Breakpoint concentration of octadecyltrimethylammonium oxalate as a function of reciprocal of dielectric constant $1/D$; (A) $100\sqrt{Cb}$, ○ acetone, ◓ methanol; (B) $\log_{10}Cb$, ⊕ acetone, ● methanol.

where the square root of the breakpoint concentration is plotted as a function of solvent composition (1, mole per cent., and 2, weight per cent. of additive). Curves A relate to acetone and Curves B to methanol. The divergence of the curves is greater on a mole than on a weight per cent. basis. It will be noted that the change in the breakpoint concentration, for a given amount of additive, increases with increasing additive content of the solvent.

The results for acetone and methanol can be brought to substantial coincidence by plotting the breakpoint concentration as a function of the reciprocal of the dielectric constant. In Fig. 5A, the square root of the breakpoint concentration is plotted as a function of the reciprocal of the dielectric constant of the mixtures. It will be noted that the points for the two solvents lie on the same curve within the limit of experimental error. In Fig. 5B, the logarithm of breakpoint concentration is plotted as a function of the reciprocal of dielectric constant. Here the points lie on the same straight line within the experimental error.

The coincidence of the values for the two solvents, when plotted as a function of $1/D$, would seem to indicate a possible connection between the breakpoint phenomenon and the dielectric constant of the solvent medium. However, such a coincidence in the present instance may be purely fortuitous. Thus, Brown[6] has shown that, with dodecylammonium chloride, methanol increases the breakpoint concentration while isopropyl alcohol and *t*-butanol decrease it.

Specific differences between acetone and methanol are more apparent in the cases of the bromate and formate than in that of the oxalate. In 10.1% methanol, the bromate does not show a maximum, while in 15.1% methanol, a maximum occurs: Λ starts to rise at about $C = 3.2 \times 10^{-4}$ and reaches its largest value at $C = 6.2 \times 10^{-4}$; the peak in Λ is about two units high.[4] The highest peak for the bromate comes at about 20% methanol (Curve 3, Fig. 3) and is about 2.5 Λ-units high. In contrast, the bromate in 10.0% acetone shows a maximum starting at $C = 2.4 \times 10^{-4}$, the largest value of Λ comes at $C = 7.3 \times 10^{-4}$, and the peak is 7 Λ-units high.

Similarly, in the case of the formate, the maximum phenomenon is more pronounced in acetone–water mixtures than it is in methanol–water mixtures. Thus, in 19.4% and 23.5% methanol, the peak for the formate is about 3.5 and 2.5 Λ-units high,[5] respectively, while for the same salt in 10.0 and 13.9% acetone the maximum is 10.7 and 7.5 Λ-units high, respectively.

In 10% acetone, the formate exhibits a higher peak than the bromate; similarly, in a given methanol–water mixture, the formate gives rise to a more pronounced maximum than does the bromate.

As far as the present investigation goes to show, it appears that a salt which exhibits a maximum in Λ in a methanol–water mixture will also show a maximum in an acetone–water mixture, but in the latter case, the start of the rise in Λ comes at a somewhat lower concentration and the height of the peak is markedly greater (perhaps by a factor of two or three). However, the salt concentration corresponding to the maximum value of Λ is about the same in the two solvent mixtures.

V. Summary

1. Measurements have been made on the conductance of octadecyltrimethylammonium oxalate in water–acetone mixtures (0 to 28.8% acetone by wt.), *n*-octadecyltrimethylammonium formate in 10.0 and 13.9% acetone and *n*-octadecyltrimethylammonium bromate in 10.0% acetone, all at 25°.

2. In water–acetone mixtures, the oxalate shows the breakpoint phenomenon; the critical concentration increases with increasing acetone content of the solvent. The results in water–acetone mixtures are similar to those previously obtained with water–methanol mixtures.

3. The curves obtained by plotting the square root of the breakpoint concentration of octadecyltrimethylammonium oxalate against the reciprocal of the dielectric constant of the solvent for water–acetone and water–methanol mixtures nearly coincide.

4. The logarithm of the critical concentration is a linear function of the reciprocal of the dielectric constant for the oxalate in water–acetone and water–methanol mixtures.

5. *n*-Octadecyltrimethylammonium formate and bromate show maxima in conductance curves for water–acetone as well as for water–methanol mixtures. The peaks for acetone are higher than for methanol.

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