mm. in comparison to 0.342 mm. obtained by extrapolation of the present data upward. The agreement is considered satisfactory in view of errors in the two methods.

The vapor pressure of hemimellitene has been measured by Smith and Spillane[11] on carefully purified material. They used the method of Smith and Lund.[9] Their data have been fitted by the API–NBS Research Project 44[10] to the Antoine equation. The extrapolations of the Antoine equation downward and the present data upward to 0° give 0.255 mm. and 0.242 mm., respectively. The agreement was considered satisfactory.

It was called to the authors' attention that the heats of vaporization calculated from equation (1), Table I, are in discrepancy with calorimetrically measured values[12] in the cases of pseudocumene and hemimellitene. The short temperature range of this investigation, the recognized errors in temperature and pressure, and the difficulty of removal of the last traces of the volatile component undoubtedly account for these discrepancies.

In order to obtain the best representation of vapor pressures over the range covered, the present data and the extrapolated calorimetric heats of vaporization were combined to fit an equation of the type

$$\log p = -(A/T) - B \log T + C \qquad (2)$$

The constants of the equations are given in Table II for the three isomeric trimethylbenzenes. The average deviations of the present data from equation (2) is also tabulated for each compound.

TABLE II

	A	B	C	Av. % deviation
Mesitylene	4106.4	12.588	45.3277	1.0
Pseudocumene	4120.6	12.588	45.3311	1.6
Hemimellitene	4182.2	12.588	45.4053	4.0

As a check on the validity of the calibration the vapor pressure of water was measured from −40 to −32°. The results were compared with the data of Scheel and Heuse,[13] who made careful measurements over the same temperature range using the Rayleigh manometer. The present vapor pressure data were about 4% higher, but slopes of the vapor pressure curves were alike. The average deviation of Scheel and Heuse's data from their calculated vapor pressure curve was 2.2% over the temperature range in question. The agreement was thus quite satisfactory.

Acknowledgments.—The authors wish to acknowledge the continued interest of Dr. Hertha Sponer at whose suggestion this investigation was undertaken.

One of us (E.R.H.) held a research assistantship which was supported by a grant-in-aid from the Duke University Research fund.

Acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of samples measured in this investigation.

Summary

1. The vapor pressures of the three isomeric trimethylbenzenes were measured in the region 0.01–1.0 mm. by a Rodebush manometer.

2. The data were fitted to the equation

$$\log_{10} P = -(A/T) + B$$

by the method of least squares.

3. The data were compared by an extrapolation method to the data of previous workers in a higher pressure range. The agreement was satisfactory.

DURHAM, N. C. RECEIVED APRIL 30, 1948

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[11] Smith and Spillane, THIS JOURNAL, 62, 2639 (1940).

[12] Osborne and Ginnings, *J. Research Natl. Bur. Standards*, 39, 453 (1947).

[13] Scheel and Heuse, *Ann. Physik*, 29, 723 (1909).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXV. Conductance of Some Long Chain Salts in Methanol–Water Mixtures[1]

BY PHILIP F. GRIEGER AND CHARLES A. KRAUS

I. Introduction

In a previous paper of this series,[2] the effect of added methanol on the equivalent conductance of long chain electrolytes in aqueous solution was described. It was found that in the case of *n*-octadecyltrimethylammonium nitrate and *n*-hexadecylpyridonium bromide, the breakpoint concentration increases with increasing methanol content of the solvent, while the critical phenomenon becomes less pronounced. On the other hand, for *n*-octadecylpyridonium chloride in methanol–water mixtures, the form of the conductance curve differs strikingly from that in water. While the usual "breakpoint" phenomenon is observed in water, in mixtures containing 10 to 35% methanol, Λ passes through a maximum at concentrations in the neighborhood of the critical concentration in water. This is apparently the first observation of such an effect in solutions of simple paraffin-chain salts.[3]

Since *n*-octadecylpyridonium bromide shows the

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[1] This paper is based on a portion of a thesis presented by Philip F. Grieger in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1947.

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

[3] Robinson and Garrett, *Trans. Faraday Soc.*, 35, 771 (1939), found maxima in the equivalent conductance of certain dyes.

usual "breakpoint" phenomenon in methanol-water mixtures, it is clear the gegenion is an important factor in determining the properties of paraffin-chain electrolyte solutions. It is probably fair to state that the prevailing view of these solutions, which is usually incorporated in the micelle theory, tends to underestimate the role of the gegenion.

The present investigation, which is an extension of the earlier work of Evers, was undertaken for the purpose of disclosing, more fully, the influence of the gegenion on the properties of solutions of long chain salts.

II. Experimental

Solvents, Apparatus and Procedure.—The details appertaining to these have been fully described in an earlier paper.[2] All measurements were made at 25 ± 0.01°.

Salts.—*n*-Octadecyltrimethylammonium iodide was prepared by the reaction of *n* octadecyl iodide with trimethylamine in aqueous ethanol solution. The reaction was carried out in a sealed tube maintained at 70° for about ten days. The crude salt (117 g.) was recrystallized six times from a variety of solvents; iodine, 28.88 ± 0.04%; theory, 28.88%.

The corresponding chloride, bromate, oxalate, iodate, bromide and nitrate were prepared by metathesis of the appropriate silver salt with *n*-octadecyltrimethylammonium iodide in absolute methanol. The salts were crystallized until their conductance in methanol or water solution remained constant.

The conductance of the chloride showed no measurable variation between four and five crystallizations; chlorine found,10.18 ± 0.02%; theory, 10.19%.

The conductance of the bromate was essentially the same after two and three cyrstallizations; bromate found, 18.13 ± 0.04%; theory, 18.14%.

There was no detectable change in the conductance of the oxalate between four and seven crystallizations. The salt was not analyzed.

The iodate was crystallized seven times in all. The difference in conductance of the salt in methanol after two and seven crystallizations was 0.2%. The conductance measurements reported below were made within a short time after final purification. On standing several months, the salt turned brown.

The bromide was crystallized three times; bromine found, 20.34 ± 0.03%; theory, 20.36%.

The formate was prepared by metathesis of potassium formate with *n*-octadecyltrimethylammonium nitrate in ethanol. A comparison of the conductance of the salt crystallized six and seven times from acetone showed a difference of 0.2%.

III. Experimental Results

In Tables I, II and III are given selected values of the equivalent conductance as a function of the square root of concentration (in equivalents per liter of solution) for *n*-octadecyltrimethylammonium chloride, bromate and oxalate, respectively. To illustrate the magnitude of the solvent correction, the numbers in parentheses show the per cent. solvent correction that was applied at the corresponding concentrations. The data presented in the tables are so chosen that large-scale graphs of the results may be prepared successfully therefrom. The values of Λ are arbitrarily given to four significant figures; in view of the large solvent corrections in the neighborhood of 1 × 10^{-4} *N*, particularly in water-rich mixtures, conductance values in the most dilute solutions may be uncertain by 1%, or more. The solvent composition is given in weight per cent. of methanol. Solvent densities, viscosities and dielectric constants were interpolated on large graphs based on the same data as those of Evers.[2] Values of these constants (viscosity in millipoise) are given at the head of each table along with the specific conductance of the solvent.

TABLE I

CONDUCTANCE OF *n*-OCTADECYLTRIMETHYLAMMONIUM CHLORIDE IN METHANOL-WATER MIXTURES AT 25°

$10^2\sqrt{C}$	Λ	$10^2\sqrt{C}$	Λ
Water		4.75% Methanol	
$\kappa_0 = 1.0 \times 10^{-6}$, d = 0.9971, η = 8.95, D = 78.5		$\kappa_0 = 0.90 \times 10^{-6}$, d = 0.9890, η = 10.4, D = 76.6	
1.144	95.93 (8)	1.431	81.69 (6)
1.365	95.21	1.598	81.07
1.422	94.62	1.674	80.83
1.548	94.13	1.849	80.69
1.706	93.79	2.001	79.54
2.132	81.17 (3)	2.222	73.57
2.227	77.70	2.587	65.25
2.652	66.79	3.169	55.99
3.244	56.97	4.014	47.44
4.180	48.56	5.353	39.73 (1)
6.265	38.91	6.131	36.8
9.568	32.46 (0.3)	7.389	33.55
17.66% Methanol		30.09% Methanol	
$\kappa_0 = 0.77 \times 10^{-6}$, d = 0.9683, η = 13.5, D = 70.9		$\kappa_0 = 0.43 \times 10^{-6}$, d = 0.9486, η = 15.5, D = 65.4	
1.502	62.76 (5)	1.616	53.78 (3)
1.643	62.88	1.817	53.72
1.889	62.89	2.180	53.53
2.054	63.13	2.367	53.51
2.195	63.50	2.594	53.50
2.397	64.26	2.882	53.53 (1)
2.604	64.51	3.191	53.61
2.848	63.85	3.578	53.75
3.172	61.77	4.199	53.75
3.443	59.39	4.744	52.92
3.814	55.88 (1)	5.743	49.51
4.192	52.41	7.415	42.88 (0.2)
4.670	48.38		
5.377	43.44		
6.104	39.50 (0.5)		
41.33% Methanol		50.33% Methanol	
$\kappa_0 = 0.40 \times 10^{-6}$, d = 0.9300, η = 15.8, D = 60.4		$\kappa_0 = 0.35 \times 10^{-6}$, d = 0.9124, η = 15.4, D = 56.2	
1.693	49.52 (4)	1.285	49.02 (3)
2.116	49.37	1.505	48.87
2.621	49.17 (1)	1.619	48.81
3.471	48.90	1.855	48.70
4.473	48.63	2.097	48.59
5.599	48.17 (0.3)	2.645	48.30 (1)
6.699	47.80	3.689	47.77
7.673	46.89	4.516	47.35
9.052	44.58 (0.1)	6.831	46.48
12.52	*37.73*	*8.628*	*45.48*
89.84% Methanol		100% Methanol	
$\kappa_0 = 0.15 \times 10^{-6}$, d = 0.8182, η = 7.90, D = 38.0		$\kappa_0 = 0.07 \times 10^{-6}$, d = 0.7866, η = 5.45, D = 32.6	
1.991	64.08 (0.6)	1.825	82.54 (0.3)
4.736	60.05 (0.1)	3.513	78.49
7.828	56.29	5.731	73.70 (0.03)
10.51	53.01	6.943	71.32
14.11	50.19	10.64	65.08

The results of Tables I, II and III, along with others not otherwise reported in this paper, are shown graphically in Figs. 2, 3, 4, 5 and 6.

In addition to the three salts for which data are presented, measurements were also carried out with: *n*-octadecyltrimethylammonium iodate and bromide in 100, 20.15 and 15.24% methanol; *n*-octadecyltrimethylammonium nitrate in water and *n*-octadecyltrimethylammonium formate in water and 19.38 and 25.51% methanol.[4] Numerical results with the above systems are not reported for the sake of brevity[5] but they are shown graphically in Figs. 1, 7 and 8.

TABLE II

CONDUCTANCE OF *n*-OCTADECYLTRIMETHYLAMMONIUM BROMATE IN METHANOL–WATER MIXTURES AT 25°

Water

$\kappa_0 = 1.0 \times 10^{-6}$, $d = 0.9971$, $\eta = 8.95$, $D = 78.5$

$10^2\sqrt{C}$	Λ
1.270	74.00 (8)
1.405	73.66
1.581	73.52
1.831	70.04
2.012	64.24 (3)
3.237	44.75
5.472	33.49 (1)

10.07% Methanol

$\kappa_0 = 0.80 \times 10^{-6}$, $d = 0.9806$, $\eta = 12.0$, $D = 74.5$

$10^2\sqrt{C}$	Λ
1.491	60.45 (6)
1.604	60.13
1.745	60.31
1.929	59.92
2.113	59.61
2.437	55.67
2.686	52.23
3.075	47.51
4.548	36.09 (1)
5.617	31.63
7.541	26.97 (0.5)

15.08% Methanol

$\kappa_0 = 0.72 \times 10^{-6}$, $d = 0.9725$, $\eta = 12.9$, $D = 72.1$

$10^2\sqrt{C}$	Λ
1.571	54.89 (5)
1.749	54.77
1.872	54.96
2.106	55.29
2.348	56.21
2.618	55.32
2.819	53.95
3.510	46.96
4.762	37.37 (1)
6.380	30.44
7.727	27.10

20.66% Methanol

$\kappa_0 = 0.73 \times 10^{-6}$, $d = 0.9634$, $\eta = 14.0$, $D = 69.7$

$10^2\sqrt{C}$	Λ
1.545	49.99 (6)
1.827	50.11
2.165	50.43
2.346	50.79
2.522	51.34
2.734	51.91
2.983	51.98
3.262	51.26
3.656	49.14 (1)
5.161	39.33
7.584	29.43

30.09% Methanol

$\kappa_0 = 0.45 \times 10^{-6}$, $d = 0.9486$, $\eta = 15.5$, $D = 65.4$

$10^2\sqrt{C}$	Λ
2.110	45.73 (2)
2.429	45.67
2.866	45.73
3.381	45.98 (1)
3.769	46.20
4.093	46.36
4.399	46.18
5.065	45.06
6.694	39.41
10.05	29.66 (0.2)

40.09% Methanol

$\kappa_0 = 0.46 \times 10^{-6}$, $d = 0.9323$, $\eta = 15.8$, $D = 60.9$

$10^2\sqrt{C}$	Λ
2.256	43.18 (2)
4.036	42.96 (0.5)
6.022	42.59
7.038	42.01
9.846	37.30 (0.1)

50.33% Methanol

$\kappa_0 = 0.35 \times 10^{-6}$, $d = 0.9124$, $\eta = 15.4$, $D = 56.2$

$10^2\sqrt{C}$	Λ
1.887	43.97 (4)
2.388	43.80
2.712	43.62 (1)
3.601	43.14
4.942	42.61
6.132	42.03
8.806	40.96 (0.1)

74.95% Methanol

$\kappa_0 = 0.17 \times 10^{-6}$, $d = 0.8567$, $\eta = 11.3$, $D = 44.9$

$10^2\sqrt{C}$	Λ
3.989	51.27 (0.2)
7.092	48.51
10.33	45.92
15.14	42.66 (0.02)

89.84% Methanol

$\kappa_0 = .015 \times 10^{-6}$, $d = 0.8182$, $\eta = 7.90$, $D = 38.0$

$10^2\sqrt{C}$	Λ
1.434	68.03 (1)
5.543	61.63 (0.1)
8.314	57.78

100% Methanol

$\kappa_0 = 0.10 \times 10^{-6}$, $d = 0.7866$, $\eta = 5.45$, $D = 32.6$

$10^2\sqrt{C}$	Λ
1.118	86.99 (1)
2.853	82.64 (0.1)
3.362	81.37
6.194	73.97

TABLE III

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

Water

$\kappa_0 = 1.0 \times 10^{-6}$, $d = 0.9971$, $\eta = 8.95$, $D = 78.5$

$10^2\sqrt{C}$	Λ
0.9125	82.51 (14)
1.012	72.19
1.117	62.39
1.3700	45.48
1.876	29.54 (10)
2.964	18.71
5.089	13.12 (2)
8.417	10.59

20.66% Methanol

$\kappa_0 = 0.73 \times 10^{-6}$, $d = 0.9634$, $\eta = 14.0$, $D = 69.7$

$10^2\sqrt{C}$	Λ
1.295	52.75 (8)
1.479	52.15
1.695	47.46
2.197	31.70
3.093	19.59 (3)
4.501	12.92
6.992	9.274

30.15% Methanol

$\kappa_0 = 0.42 \times 10^{-6}$, $d = 0.9484$, $\eta = 15.5$, $D = 65.4$

$10^2\sqrt{C}$	Λ
1.678	47.93 (3)
2.087	47.65
2.354	47.73
2.780	42.35
3.653	27.76 (1)
5.019	17.17
8.137	10.39

40.09% Methanol

$\kappa_0 = 0.46 \times 10^{-6}$, $d = 0.9323$, $\eta = 15.8$, $D = 60.9$

$10^2\sqrt{C}$	Λ
2.531	43.88 (2)
2.968	43.75 (1)
3.762	43.20
4.152	42.85
4.840	40.81
6.685	25.92
9.997	14.89 (0.3)

50.33% Methanol

$\kappa_0 = 0.35 \times 10^{-6}$, $d = 0.9124$, $\eta = 15.4$, $D = 56.2$

$10^2\sqrt{C}$	Λ
1.733	44.37 (2)
2.404	44.10
3.650	43.25
5.582	41.45
6.571	40.43 (0.5)
8.558	36.96
10.36	30.18
13.89	20.65 (0.1)

89.84% Methanol

$\kappa_0 = 0.15 \times 10^{-6}$, $d = 0.8182$, $\eta = 7.90$, $D = 38.0$

$10^2\sqrt{C}$	Λ
1.976	61.70 (0.6)
5.897	51.66 (0.1)
10.51	43.29
14.12	38.90

100% Methanol

$\kappa_0 = 0.08 \times 10^{-6}$, $d = 0.7866$, $\eta = 5.45$, $D = 32.6$

$10^2\sqrt{C}$	Λ
1.896	73.68 (0.3)
4.859	61.33 (0.1)
6.837	54.80
8.973	49.29

IV. Discussion

1. Importance of the Gegenion.—It has long been recognized that the critical phenomena in solutions of long chain salts is dependent on

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[4] Measurements with these two mixtures were carried out and reported by Dr. C. J. Carignan, Thesis, Brown University, 1947.

[5] For numerical data, consult Ref. 1.

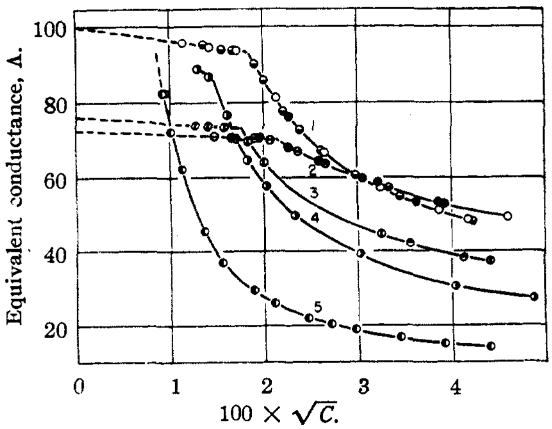

Fig. 1.—Conductance curves for octadecyltrimethylammonium salts in water: curve (1) chloride, (2) formate, (3) bromate, (4) nitrate, (5) oxalate.

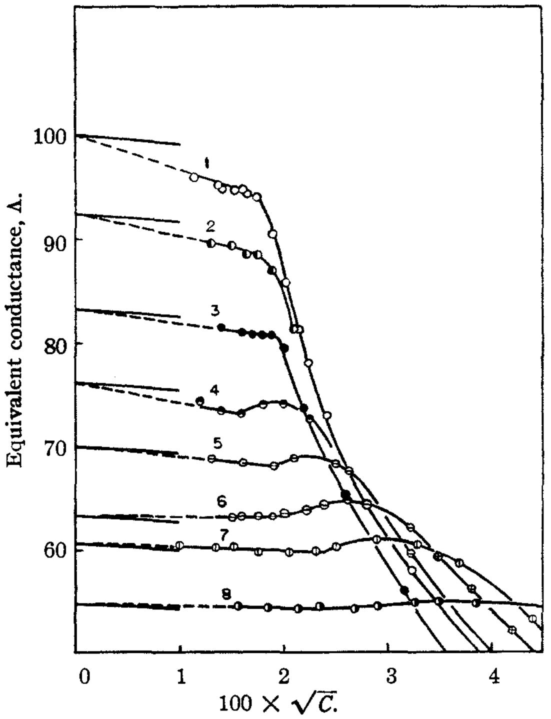

Fig. 2.—Curves for octadecyltrimethylammonium chloride in methanol-water mixtures: Methanol for curve (1) 0%, (2) 2.31%, (3) 4.74%, (4) 10.07%, (5) 12.90%, (6) 17.66%, (7) 22.14%, (8) 30.09%; solid lines indicate Onsager slope.

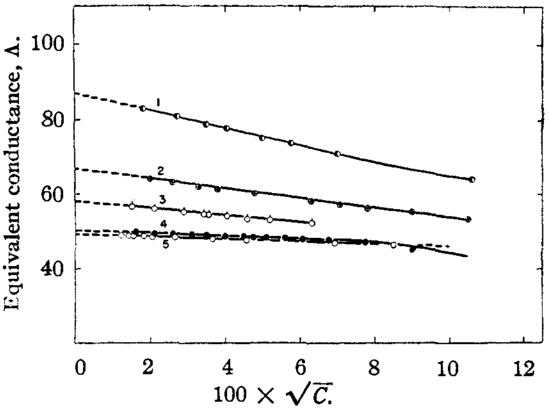

Fig. 3.—Curves for octadecyltrimethylammonium chloride in methanol-water mixtures: methanol for curve (1) 100%, (2) 89.84%, (3) 80.06%, (4) 41.33%, (5) 50.33%.

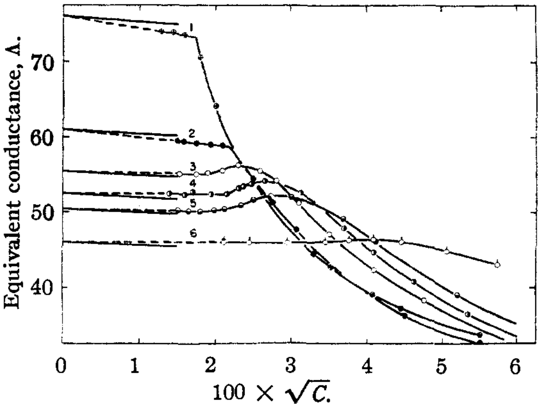

Fig. 4.—Curves for octadecyltrimethylammonium bromate in methanol-water mixtures: methanol for curve (1) 0%, (2) 10.07%, (3) 15.08%, (4) 18.54%, (5) 20.66%, (6) 30.09%; solid lines indicate Onsager slope.

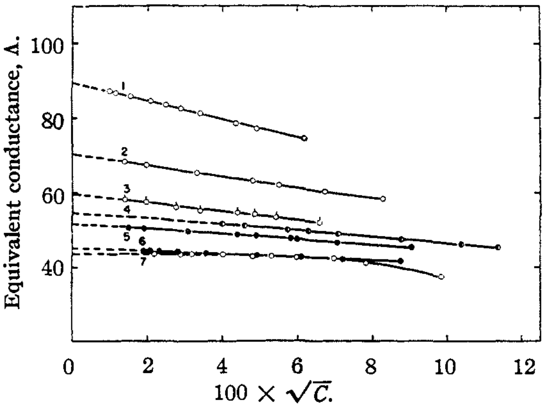

Fig. 5.—Curves for octadecyltrimethylammonium bromate in methanol-water mixtures: methanol for curve (1) 100%, (2) 89.84%, (3) 80.06%, (4) 74.95%, (5) 69.80%, (6) 50.33%, (7) 40.09%.

the length of the hydrocarbon chain; as the chain length is increased, the breakpoint appears at lower concentrations. However, it has not been generally recognized that the critical phenomenon is also markedly dependent on the nature of the gegenion. More striking, perhaps, is the fact that in methanol-water mixtures, as well as in water,[6] the form of the curve in the critical region is primarily determined by the gegenion. Thus, for some salts, a normal breakpoint is observed; for others, a maximum is found.

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(6) Brown, Grieger, Evers and Kraus, THIS JOURNAL, 69, 1835 (1947).

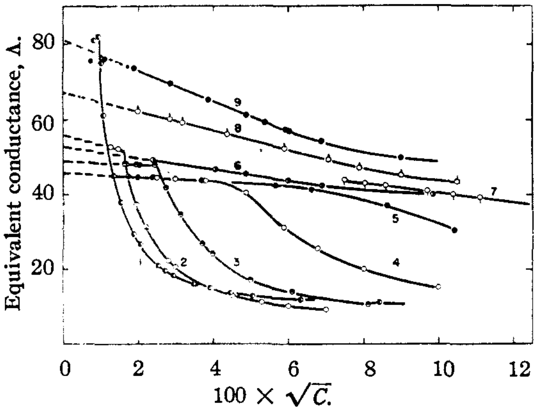

Fig. 6.—Curves for octadecyltrimethylammonium oxalate in methanol-water mixtures: methanol for curve (1) 0%, (2) 20.66%, (3) 30.15%, (4) 40.09%, (5) 50.33%, (6) 69.80%, (7) 74.95%, (8) 89.84%, (9) 100%.

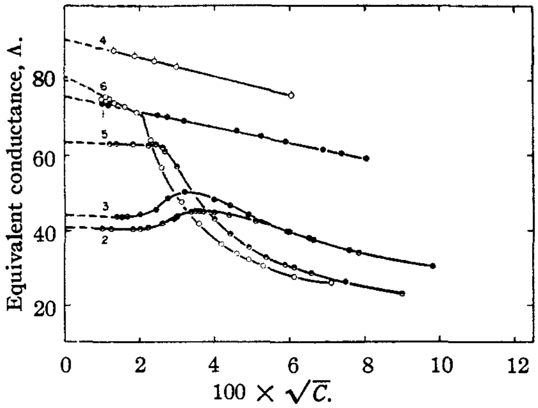

Fig. 7.—Curves for salts in methanol-water mixtures, octadecyltrimethylammonium iodate: methanol for curve (1) 100%, (2) 20.15%, (3) 15.24%; octadecyltrimethylammonium bromide: methanol for curve (4) 100%, (5) 20.15%, (6) 15.24%.

In Fig. 1 are shown conductance curves for five different octadecyltrimethylammonium salts in water, all of which show a breakpoint. The values of the breakpoint concentration are given in Table IV. In the case of the oxalate, the breakpoint was not reached at the lowest concentrations measured, 0.9 × 10^{-4} *N*.

TABLE IV

CRITICAL CONCENTRATION OF *n*-OCTADECYLTRIMETHYLAMMONIUM SALTS IN WATER AT 25°

Gegenion	Critical concn. × 10^4	Curve type in mixtures	$-d\Lambda/d\sqrt{C}$ × 10^{-3} from higher concn.
Oxalate	<1	No max.	11.3
Nitrate	2.3	No max.	7.6
Bromate	3.1	Max.	5.0
Chloride	3.4	Max.	5.0
Formate	4.4	Max.	1.1

The ratio of the critical concentrations of the formate and nitrate is about two. On the other hand, the critical concentrations of two homologous long chain salts, that differ by two carbon atoms in the chain, stand in the ratio of about one to two or three. For example, the critical concentrations of *n*-octadecylammonium chloride and *n*-hexadecylammonium chloride in water at 60° are 5.3 × 10^{-4} *N* and 9.7 × 10^{-4} *N*, respectively.[7] The variation of the critical concentration with gegenion can hardly be classed as a second order effect.

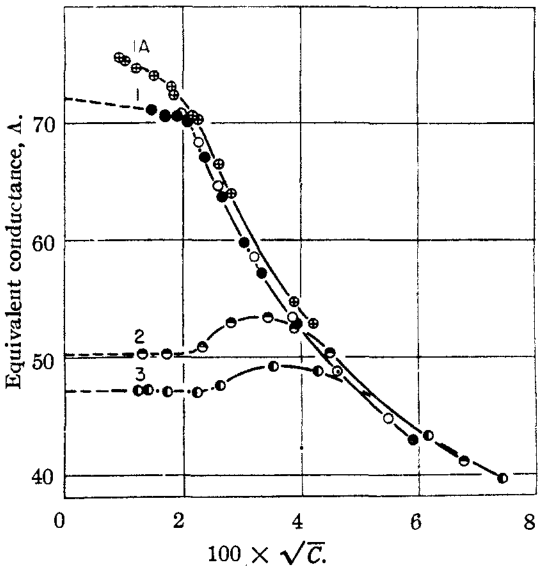

Fig. 8.—Curves for octadecyltrimethylammonium formate in methanol-water mixtures: methanol for curve (1) 0%, (1A) 0% (Thompson), (2) 19.38%, (3) 25.51%.

In methanol–water mixtures, even more pronounced differences in behavior are found. Thus, the chloride, bromate, iodate and formate (Figs. 2, 4, 7 and 8) exhibit maxima in Λ in solvent mixtures containing approximately 10–35% of methanol, while the nitrate,[2] oxalate and bromide (Figs. 6 and 7) show normal breakpoints.

There appears to be a fair correlation between the tendency to exhibit a maximum in Λ in these mixtures and the mobility of the gegenion in water. The three slower of the ions tested, namely, the iodate, formate and bromate, all show the maximum phenomenon. Among the relatively fast ions tested, only the chloride shows this effect. A somewhat better correlation exists between the tendency to form a maximum and the critical concentration in water; the tendency decreases with decrease in critical concentration.

It is of interest to note in this connection that the slope of the curve, $-d\Lambda/d\sqrt{C}$, at the critical concentration (approached from the high concentration side), in general, decreases markedly as the critical concentration and tendency to form a maximum increases. These slopes are listed in Table IV, column 4.[8]

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[7] Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942); Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

[8] G. L. Brown, Thesis, Brown University, 1947.

2. Effect of Ion Structure.—The breakpoint concentration appears to be markedly dependent on the structure of the quaternary ammonium ion. This will be evident on inspection of Table V in which are given breakpoint concentrations for octadecyltrimethylammonium and octadecylpyridonium chloride and nitrate in water.

TABLE V

COMPARISON OF BREAKPOINT CONCENTRATIONS IN WATER FOR DIFFERENT CATIONS WITH THE SAME ANION

Salt	C (crit.) × 10^4
$C_{18}H_{37}C_5H_5NCl$ (2)	2.4
$C_{18}H_{37}(CH_3)_3NCl$	3.4
$C_{18}H_{37}\cdot C_5H_5NNO_3$ (2)	1.3
$C_{18}H_{37}(CH_3)_3NNO_3$	2.3

It will be noted that, in the case of the chloride, the breakpoint concentration of the trimethyl derivative is 40% greater than that of the corresponding pyridonium salt; for the nitrates, it is nearly twice as great. It is clear that the critical phenomenon in the case of long chain salts is markedly influenced by the nature and (probably) size of the organic groups associated with the nitrogen of the quaternary ammonium ion.

3. Effect of Methanol on the Critical Concentration.—In general, the critical concentration for a given octadecyltrimethylammonium salt increases with increasing methanol content of the solvent. For small additions of methanol, up to a few per cent., as in the case of octadecyltrimethylammonium chloride, there may be a slight initial decrease of the critical concentration. For somewhat larger additions, however, there is an increase. With a methanol content above 10–15%, a maximum occurs in the conductance curve of the chloride and we can no longer speak of a breakpoint. Evers[2] has found a marked increase in the breakpoint concentration with increasing methanol content in the case of octadecylpyridonium bromide as well as with octadecyltrimethylammonium nitrate. As may be seen from Fig. 6, the breakpoint concentration for octadecyltrimethylammonium oxalate is greatly increased on addition of methanol, some forty times for a 50% mixture.

The manner in which methanol affects the maximum is of much interest. In the case of both octadecyltrimethylammonium chloride and bromate (Figs. 2 and 4), small additions of methanol cause little more than a slight displacement of the breakpoint concentration. The curve for the chloride at 4.74% methanol may exhibit an incipient maximum; at 10% methanol, however, it has a pronounced maximum. The curve for the bromate, on the other hand, has a normal breakpoint for a 10% methanol mixture, but for a 15% mixture, it exhibits a pronounced maximum.

With increasing methanol content of the solvent, the point at which the conductance curve begins to rise above the straight line of the more dilute solutions shifts somewhat toward higher concentrations but the bow of the maximum widens greatly. The maximum is most pronounced at approximately 20% methanol; at 30%, the maximum has almost disappeared. With the chloride and the bromate, there is no evidence left of the maximum effect in a 50% methanol solvent but with the oxalate, the effect of the critical phenomenon still persists (as shown by the drop in the curve) for a solvent of this methanol content (curve 5, Fig. 6).

It is evident that the nature of the gegenion has a marked effect on the properties of long chain salts in the critical region, particularly on the development of a conductance maximum. It will be shown in a later communication that the maximum phenomenon is also sensitive to the length of the hydrocarbon chain.[9]

4. Limiting Slopes.—Whether or not the slopes of the conductance curves of long chain electrolytes in aqueous solution approach theoretical values in the limit, as concentration decreases, remains uncertain on the basis of existing data. The difficulty lies in that experimental errors increase greatly as the concentration approaches very low values ($< 1 \times 10^{-4}$), while deviations from the limiting theoretical behavior become increasingly great as concentration increases. An additional difficulty arises owing to the fact that the critical concentration for many long chain electrolytes lies at very low values. The question can be resolved only by measurements of highest precision carried to concentrations approaching 1×10^{-5} N, in some instances. It may be noted that Scott and Tartar[9] found the conductance curve for hexadecyltrimethylammonium bromide closely approximating the theoretical slope at very low concentrations.

The slope of conductance curves in methanol and methanol-rich water mixtures, so far as presently approximated, are generally somewhat greater than (but near) the theoretical value. In computing the theoretical slope, values of Λ_0 were employed that were found from the experimental data by extrapolation. A given percentage error in the value of Λ_0 results in approximately one-third that error in the value of the computed slope. The Λ_0 value of the oxalate ion used in these computations is based on the value 35.4 for the conductance of the octadecyltrimethylammonium ion in methanol (Sec. 5, below).

The observed and theoretical slopes for a number of salts in pure methanol are compared in Table VI. The deviations from the theoretical slope down to 80% methanol differ little from those for pure methanol as given in this table.

As may be seen from column 5 of the table, the slope in all cases, with the exception of the iodate and the oxalate, is slightly above the theoretical. The small differences found may be due either to experimental error or to very slight ion-pair asso-

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(9) Scott and Tartar, THIS JOURNAL, 65, 692 (1943).

TABLE VI

COMPARISON OF SLOPES FOR OCTADECYLTRIMETHYLAMMONIUM SALTS IN PURE METHANOL

Salt	Λ_0	Obs. slope	Theor. slope	Δ Slope, %
Chloride	86.8	235	226	4
Bromate	89.6	249	229	9
Bromide	90.7	245	230	6
Iodate	75.7	212	217	−2
Oxalate	81.4	410	440	−7

ciation. In its ion-pair interaction, the long chain ion with three methyl groups differs little from the tetramethylammonium ion and a small amount of interaction is to be expected on the basis of the dielectric constant of methanol. While the slope for the oxalate is somewhat below the theoretical, which may be due to experimental error, it is of interest to note that a 2,1-salt approximates the theoretical slope so closely in methanol. The iodate approximates the theoretical value closely.

For methanol–water mixtures of intermediate methanol content (in the neighborhood of 50%) the observed slopes become less than the theoretical, in some instances, less than one half that value. On referring to Figs. 2 and 4 for octadecyltrimethylammonium chloride and bromate, respectively, it will be seen that experimental curves begin to lie above the theoretical straight lines at 15 to 18% of methanol. The curves reach their lowest slope at 40 to 50% methanol as may be seen from Fig. 3, curves 4 and 5, and Fig. 5, curves 6 and 7. A similar situation is found in the case of octadecyltrimethylammonium oxalate, Fig. 6, curves 4 and 5. It is a striking fact that for these solutions, the observed conductances lie on a straight line over an extended range of concentration; in the case of octadecyltrimethylammonium chloride in a 41% methanol-water mixture (Fig. 3, curve 4), from 2.9×10^{-4} *N* to 45×10^{-4} *N*. For a 50% methanol mixture with the same salt (Fig. 3, curve 5), the points lie on a straight line from 1.6×10^{-4} to 70×10^{-4}. Similar results are found for the bromate in the same methanol mixtures.

How greatly the observed slopes differ from the theoretical values will be apparent from Table VII in which values of observed and theoretical slopes are given for the chloride and the bromate in 40 and 50% methanol mixtures.

TABLE VII

COMPARISON OF SLOPES FOR OCTADECYLTRIMETHYLAMMONIUM SALTS IN 40 AND 50% METHANOL MIXTURES

Salt	% CH_3OH	Λ_0	Obs. slope	Theor. slope
Chloride	41.3	50.0	34	56
Chloride	50.3	49.4	51	60
Bromate	40.1	43.5	18	53
Bromate	50.3	44.9	47	58

It will be noted that the discrepancy is greatest for the 40% mixture, the observed value for the bromate being only one-third the theoretical.

The rectilinear form of the curves over a large concentration range and the low value of their slopes cannot well be ascribed to experimental error. As may be seen from Tables I and II, the solvent correction was, at most, 4%; to account for linearity in dilute solutions would require an over correction for the solvent by as much as 60%. Solvent conductances do not usually decrease in the course of a series of experiments and, in the present instance, such a decrease would seem to have been precluded by the conditions under which the measurements were carried out. Moreover, if over or under corrections are made for the solvent, the points do not lie on a straight line; they diverge increasingly below or above the straight line as determined by values at higher concentration where corrections for solvent conductance are negligible.

We may conclude that the results for methanol–water mixtures in the neighborhood of 50% methanol content are valid and, therefore, that: (1) the experimental conductance values conform to a linear relation in terms of the square root of concentration up to unexpectedly high concentrations; and (2) the slope of the conductance curves to the lowest concentration measured is less than the theoretical.

We can reconcile these inconsistencies by assuming that in the methanol mixtures under consideration, the long chain salts are not normal electrolytes. The proper limiting slope has not been attained because the concentrations down to which observations have been carried were not sufficiently low. The breakpoint concentration for the chloride and bromate in water are, respectively, 3.4×10^{-4} and 3.1×10^{-4} *N*. These concentrations are only little above the lowest concentrations to which measurements were carried in the methanol–water mixtures. While the breakpoint (or, in some instances, at higher methanol content, the maximum) moves toward higher concentrations with increasing methanol content, it is not safe to assume that, up to the breakpoint or the beginning of the rise toward the maximum, the long chain electrolytes have the properties of a normal electrolyte. As yet, it has not been established whether or not the tangent to the conductance curve actually goes through a discontinuity; nor do we know whether or not a discontinuity occurs in systems which exhibit a maximum. For solutions in mixtures of higher methanol content the tangent seems to vary continuously through the maximum as illustrated in Fig. 4, curve 6. Much the same condition seems to hold for salts that exhibit no maximum in methanol-water mixtures. This is clearly shown in the case of hexadecylpyridonium bromide in a 35% methanol mixture as determined by Evers.[2] It will be noted that for 40% methanol mixtures, the curves for octadecyltrimethylammonium chloride and bromate, which follow a linear relation from the lowest concentrations, fall off markedly but continuously at a concentration in the neighborhood of 7×10^{-3} *N;* when this occurs, the salts cannot be normal electrolytes.

The long concentration range over which the conductance curves of solutions of long chain salts in 40 to 50% methanol mixtures follow the square root law at below theoretical slope appears to be due to residual effects characteristic of long chain salts which have not, as yet, completely disappeared. It is to be anticipated that if sufficiently accurate measurements could be carried to sufficiently low concentration, a normal slope would be obtained.

5. Ion Conductances.—Ion conductances, as derived from a number of different salts with a common ion, serve as an excellent check on the reliability of conductance data. In methanol, Hartley[10] reports 51.3 and 55.5 for the conductance of the chloride and the bromide ion, respectively. From the plots for octadecyltrimethylammonium chloride and bromide, we obtain 86.8 and 90.7 for the limiting conductance of these two salts, respectively, whence the conductance of the octadecyltrimethylammonium ion is found to be 35.5 and 35.2. These values are in agreement within the limit of experimental error.

We have another check on the reliability of the value found for the conductance of octadecyltrimethylammoniumion by considering the conductance viscosity product, $\Lambda_0{}^+\eta$. Pickering[11] has determined the conductance of various long chain ions in several different solvents. For the $\Lambda_0{}^+\eta$ product for octadecyltrimethylammonium ion in nitrobenzene, he reports the value 0.190. Using 35.4 for the conductance of this ion in methanol, we obtain 0.193 for the conductance–viscosity product. It seems, therefore, that octadecyltrimethylammonium chloride and bromide are normal electrolytes in methanol.

When it comes to aqueous solutions of octadecyltrimethylammonium salts, it becomes difficult to properly evaluate ion conductances because of uncertainties in extrapolating for Λ_0. If the experimental conductance values for octadecyltrimethylammonium chloride, bromate and formate are extrapolated to zero concentration according to the usual square root of concentration plot, values obtained for Λ_0 are 99.5, 76.0 and 72.5, respectively. Assuming 76.3, 55.8[12] and 54.7[13] for the conductance of the anions, we obtain, respectively, 23.2, 20.3 and 17.8 for the conductance of the cation. Obviously, the values found for Λ_0 by the above method of extrapolation are greatly in error.

Another procedure is to assume that these electrolytes are normal and that the experimental values in dilute solutions are in error. The critical concentration and conductance may be determined with a fair degree of certainty. It would seem then that if a line were drawn from near the critical concentration at an angle corresponding to the theoretical slope, it should intercept the Λ axis at nearly the correct point and should yield an acceptable value of Λ_0. This is particularly the case if the critical point lies at a sufficiently low concentration, well below 1×10^{-3} *N*. On this basis, we obtain for the chloride, bromate and formate the Λ_0 values 95.0, 74.5 and 72.2, respectively. Subtracting the conductance of the negative ions as above, we obtain for the conductance of the octadecyltrimethylammonium ion the values: 18.7, 18.7 and 17.5, respectively. The agreement here is much better than when the extrapolations were carried through the experimental points.

Scott and Tartar[10] have measured the conductance of hexyltrimethylammonium and hexadecyltrimethylammonium bromide to low concentration and found the curves closely conforming to the theoretical slope. They obtained the limiting conductances 110.5 and 97.2 for the two salts, respectively; for the cations, this gives the $\Lambda_0{}^+$ values 32.2 and 18.9. If the ion conductances are multiplied by the viscosity of water, we obtain, respectively, 0.288 and 0.169 for the $\Lambda_0{}^+\eta$ product. Assuming 18.3 as the conductance of the octadecyltrimethylammonium ion, we obtain 0.164 for this product.

6. Viscosity Relations.—Lacking values for transport numbers for salts in methanol–water mixtures, it is not possible to determine how the conductance of ions varies with viscosity in these mixtures. However, the total conductance of the electrolyte is of some interest. The viscosity of water is increased markedly on addition of methanol, reaching a maximum at about 40% of methanol. On initial addition of methanol, the conductance viscosity product for long chain salts either changes but little or passes through a maximum. The $\Lambda_0\eta$ curve for octadecyltrimethylammonium bromate has a slight maximum at about 10% methanol; the values are 0.744 and 0.680 for the mixture and for water, respectively. For the corresponding chloride, $\Lambda_0\eta$ changes but little for the first 13% of methanol. Maxima of this type have been observed for certain inorganic salts in methanol–water mixtures. Thus, Longsworth and MacInnes[14] found a maximum in $\Lambda_0{}^+\eta$ for the lithium ion in the neighborhood of 16% methanol. Similar effects have been observed by Connell, Hamilton and Butler[15] with several alkali metal salts in ethanol–water mixtures.

Considering all the available facts in connection with dilute solutions of long chain salts in pure solvents, the preponderance of evidence inclines toward the view that these solutions conform to the laws of ordinary electrolytes.

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[10] Murray-Rust and Gatty, MacFarlane and Hartley, *Ann. Reports, Chem. Soc.*, **27**, 351 (1930).

[11] H. L. Pickering, Thesis, Brown University, 1947.

[12] Jones, THIS JOURNAL, **66**, 115 (1944).

[13] Saxton and Darken, *ibid.*, **62**, 846 (1940).

[14] Longsworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

[15] Connell, Hamilton and Butler, *Proc. Roy. Soc. (London)*, **147A**, 418 (1934).

7. Effect of Impurities.—The purification of long chain salts is often difficult and many of the criteria of purity that may readily be applied with ordinary salts become doubtful or break down entirely. In the end, the best criterion of the purity of a long chain electrolyte is the reproducibility of its conductance in solution. But, even here, uncertainties creep in, for we have little knowledge of how impurities may affect the conductance of such solutions. At times, the presence of small amounts of impurities may affect the character of the phenomena in the critical region without greatly altering the conductance curve at higher concentrations.

This is illustrated by curves 1 and 1A of Fig. 8 for octadecyltrimethylammonium formate in water at 25°. Curve 1 is for a sample of the formate which was prepared and purified in connection with the present investigation; curve 1A is for a salt prepared and measured by Dr. W. E. Thompson[16] in connection with an earlier investigation. It will be noted that at concentrations above the critical, the curves parallel each other closely and differ but little. In the critical region, however, there is a marked difference; the salt of the present investigation exhibits a sharp break while that of Thompson shows a continuous change in the tangent through the critical region. At low concentration, Thompson's values are approximately 5% higher while at higher concentration, they are only about 2% higher than those of our own preparation.

All this serves to emphasize the importance of purity of substances used for investigation. It also indicates the need for systematic investigation of small additions of other electrolytes, and perhaps other substances, on the properties of long chain salts.

V. Summary

1. The conductance of *n*-octadecyltrimethylammonium chloride, bromate and oxalate has been measured in 0 to 100% methanol–water mixtures at 25°. Results are also presented (graphically) for *n*-octadecyltrimethylammonium iodate and bromide in 15 to 100% mixtures, for the formate in 0 to 23.5% mixtures, and for the nitrate in water.

2. The conductance curves for the chloride, bromate, iodate and formate exhibit maxima in methanol–water mixtures; those for the oxalate, bromide and nitrate exhibit normal breakpoints.

3. The characteristic effects of long chain salts become less pronounced as the methanol content of the solvent reaches 30%; they ultimately disappear entirely.

4. The limiting slopes of the $\Lambda-\sqrt{C}$ plots closely approximate theoretical values in pure methanol and in 80% methanol–water mixtures.

5. For 40 to 50% mixtures, the plots are linear over an exceptionally large range of concentration and their slopes are markedly below their theoretical values. It is suggested that the characteristic effects of long chain salts have not, as yet, disappeared in these mixtures at the concentrations measured.

6. If conductance values for octadecyltrimethylammonium chloride, bromate and formate are extrapolated from the critical point to zero concentration, according to the theoretical slope for aqueous solutions, reasonably concordant values (18.7, 18.7 and 17.5) are obtained for the conductance of the *n*-octadecyltrimethylammonium ion in water. The conductance viscosity product becomes 0.164 on the basis of 18.3 for Λ_0^+; the values of the product for the hexadecyltrimethylammonium ion, based on Scott and Tartar's value of the conductance of its bromide, is 0.169.

7. The $\Lambda_0\eta$ product of long chain salts either shows a slight maximum in the neighborhood of 10% methanol or undergoes little change up to this content of methanol.

8. It is pointed out that the properties of solutions of a long chain electrolyte are markedly dependent on the nature of the gegenion as well as upon the structure of the long chain quaternary ammonium ion.

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[16] W. E. Thompson, Thesis, Brown University, May, 1941.