

Comparison of experiments 16 and 45 indicates that k_2 does not vary significantly with μ over the interval 0.4 to 0.8.

Acknowledgments.—The author is indebted to the late Professor William C. Bray, of the University of California, not only for suggesting this problem, but also for his encouragement and guidance during the preliminary work which ultimately led to the present investigation. Thanks are gratefully given to: Armando A. Rodrigues, Edgar Howard, Jr., and Wallace Hay for their assistance in carrying out the experiments, and to Professor Paul C. Cross and to Robert P. Epple for their review of the manuscript.

Summary

1. The rate of the chlorate-bromide reaction in the presence of arsenious acid has been investigated at high ionic strength at 25°. In the absence of arsenic acid, the rate (initial) is given

by $k_1(\text{ClO}_3^-)(\text{Br}^-)(\text{H}^+)^2$ with $k_1 = 3.0 \times 10^{-4}$.

2. Arsenic acid catalyzes the reaction. Arsenious acid and arsenate ion do not.

3. At low (H^+) and (H_3AsO_4), the catalytic action of arsenic acid can be represented fairly well by the term $k_2(\text{ClO}_3^-)(\text{Br}^-)(\text{H}^+)(\text{H}_3\text{AsO}_4)$ where $k_2 = 4.0 \times 10^{-3}$.

4. At moderate (H^+) and (H_3AsO_4), the rate of reaction is significantly higher than computed from the sum of the (fourth order) k_1 and k_2 terms. These deviations can be accounted for by adding to the rate law two more terms (fifth order), namely, $k_3(\text{ClO}_3^-)(\text{Br}^-)(\text{H}^+)(\text{H}_3\text{AsO}_4)$ and $k_4(\text{ClO}_3^-)(\text{Br}^-)(\text{H}^+)(\text{H}_3\text{AsO}_4)^2$, where $k_3 = 4.0 \times 10^{-3}$ and $k_4 = 3.0 \times 10^{-3}$.

5. The values of the rate constants listed above appertain to high ionic strengths. The numerical values of the constants do not vary significantly for ionic strengths in the neighborhood of 0.8.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXIV. Conductance of Some Long Chain Electrolytes in Methanol-Water Mixtures at 25°¹

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I. Introduction

The present paper is the first of a series of articles reporting the results of investigations of the conductance and some other properties of long chain electrolytes in aqueous solution, as well as in mixtures of water and methanol and other solvents. Specifically, in the present investigation, conductance measurements were carried out with mixtures of methanol and water, as well as with the pure solvents, for the purpose of determining how the form of the conductance function changes on going from an aqueous solution, which exhibits the characteristic breakpoint phenomenon, to a solution in a non-aqueous solvent in which no anomalies appear.³

During the course of the present investigation, Ward³ reported the results of studies on the conductance of sodium dodecylsulfate in ethanol-water mixtures. More recently, Ralston and Hoerr⁴ have examined the conductance of dodecylammonium chloride in the same solvent mixtures. Our results with *n*-hexadecylpyridonium bromide

and *n*-octadecyltrimethylammonium nitrate in methanol-water mixtures are similar to those of Ralston and Hoerr. However, we have found that with *n*-octadecylpyridonium chloride, a maximum occurs in the $\Delta-\sqrt{C}$ curves in certain mixtures of methanol and water at concentrations where a breakpoint might normally be expected. Since none of the other salts yielded a maximum, the result with the chloride is highly significant in that it indicates the importance of the gegenion in determining the state of the solution, a factor which has not been stressed in previous discussions of solutions of long chain electrolytes. In this connection, it may be noted that recent investigations in this Laboratory have disclosed that with certain combinations of long chain ions and inorganic gegenions, for example, *n*-octadecylpyridonium iodate, a maximum occurs in the conductance curve for solutions in pure water.⁴ Recently, Ralston, Eggenberger and Du Brow⁵ have found maxima for aqueous solutions of quaternary ammonium chlorides having two long chain alkyl groups in the cation.

II. Experimental

A. Apparatus and Procedure.—Mixed solvents were made up by the weight method and their methanol content is reported in weight per cent. of methanol. In making

(1) This paper comprises a portion of a thesis presented by E. Charles Evers in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1941.

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(3) Ward, *J. Chem. Soc.*, 1, 522 (1939); *Proc. Roy. Soc. (London)*, **176A**, 512 (1940); Ralston and Hoerr, *THIS JOURNAL*, **68**, 2460 (1948); Thompson and Kraus, *ibid.*, **69**, 1016 (1948); Weaver and Kraus, *ibid.*, **70**, 1707 (1948).

(4) Brown, Grieger, Evers and Kraus, *ibid.*, **69**, 1835 (1947); G. L. Brown, Thesis, Brown University, 1947.

(5) Ralston, Eggenberger and Du Brow, *ibid.*, **70**, 977 (1948).

calculations, the densities of the solutions have been assumed to be those of the solvents; the error resulting from this simplification is negligible in the more dilute regions with which we are primarily concerned. Buoyancy corrections have not been applied since the densities of solvents differed but little from the densities of salts and the correction comes within the limit of experimental error. Densities of some of the solvent mixtures were measured in this laboratory but most of the values were taken from the literature. These data were plotted on a large scale graph and the values used in making calculations were interpolated on this plot.⁶

The viscosity⁷ and the dielectric constant⁸ of the various mixtures were interpolated from the data gathered from the literature.

A correction was made for the specific conductance of the solvent when significant. The correction usually amounted to several per cent. in the more dilute solutions. Since the electrodes were not platinized, polarization corrections amounted to as much as 0.3% in the more concentrated solutions, but the correction was less than 0.1% in the more dilute solutions. Methods of preparing the solutions and measuring their resistance have been described adequately in previous numbers of this series; all measurements were carried out in an oil-filled thermostat at $25 \pm 0.01^\circ$.

A property of these solutions which seems worth mentioning is their inability to wet glass properly at salt concentrations near and below the breakpoint. This often becomes troublesome, since bubbles produced upon shaking the solutions tend to adhere to the electrode surfaces as well as the glass. However, solutions at concentrations higher than that of the breakpoint wet surfaces normally. These facts appear to be associated with the state of the solute in these solutions.

B. Solvents.—Distilled water from the laboratory supply ($\kappa = 1.6 \times 10^{-6}$ mho) was distilled from an alkaline permanganate solution contained in a copper boiler

TABLE I

n-HEXADECYLPYRIDONIUM BROMIDE IN METHANOL-WATER MIXTURES AT 25°

$\sqrt{C} \times 10^2$	λ	$\sqrt{C} \times 10^2$	λ
Water		6.36% Methanol	
$d = 0.9971, D = 78.5$		$d = 0.9867, D = 76.0$	
$\eta = 0.00895, \kappa_0 = 0.82 \times 10^{-6}$		$\eta = 0.0109, \kappa_0 = 0.83 \times 10^{-6}$	
1.397	98.14	1.835	83.29
1.562	97.74	2.046	83.03
1.708	97.46	2.243	83.15
2.105	96.84	2.470	82.83
2.566	91.03	2.854	79.56
2.791	83.65	3.735	59.15
3.124	73.38	5.300	41.80
4.249	52.49	7.797	31.36
6.148	38.64	8.829	29.14
9.554	29.95		
11.66	27.37		

(6) Longworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939); Uchida and Kato, *J. Soc. Chem. Ind. Japan*, **37**, 525B (1934); E. C. Evers, Thesis, Brown University, 1941; (a) Dittmar and Fawsitt, *Trans. Roy. Soc. Edinburgh*, **33**, 509 (1887) and (b) Circular No. 19, Bureau of Standards (1924), values at 25° obtained by graphical extrapolation of 9.7° and 19.7° values (a) combined with 15° values (b); Harned and Thomas, *THIS JOURNAL*, **57**, 1667 (1935).

(7) Longworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939); Dunstan and Thole, *J. Chem. Soc.*, **90**, 1556 (1909); Tammann and Pilsbury, *Z. anorg. allgem. Chem.*, **172**, 243 (1928), values at 25° obtained from 10, 20 and 30° values by graphical interpolation; Hartley and Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(8) Jones and Davies, *Phil. Mag.*, **28**, 307 (1939); Albricht and Gostling, *THIS JOURNAL*, **68**, 1061 (1946).

14.70% Methanol		19.91% Methanol	
$d = 0.9731, D = 72.4$		$d = 0.9645, D = 70.1$	
$\eta = 0.0129, \kappa_0 = 0.62 \times 10^{-6}$		$\eta = 0.0139, \kappa_0 = 0.55 \times 10^{-6}$	
2.330	68.50	2.845	62.62
2.601	68.13	3.202	62.40
2.952	67.94	3.670	62.09
3.366	67.48	3.967	61.98
3.538	65.42	4.330	59.28
3.750	62.63	5.378	48.76
4.167	56.49	7.162	36.88
5.532	42.32	9.182	33.98
6.718	34.43	11.35	25.79
9.177	28.08	13.44	23.43
11.50	24.75		
26.02% Methanol		35.20% Methanol	
$d = 0.9550, D = 67.4$		$d = 0.9400, D = 63.3$	
$\eta = 0.0149, \kappa_0 = 0.56 \times 10^{-6}$		$\eta = 0.0158, \kappa_0 = 0.39 \times 10^{-6}$	
2.459	57.77	2.376	53.02
3.611	57.42	3.523	52.57
4.427	57.21	5.226	51.88
5.904	52.35	6.093	51.50
6.990	45.40	7.285	50.66
7.974	40.10	8.433	48.58
9.239	34.98	9.532	45.33
11.03	29.99	11.09	40.38
14.24	24.88	13.47	34.24
54.14% Methanol		Methanol	
$d = 0.9093, D = 54.6$		$d = 0.7866, D = 32.6$	
$\eta = 0.0149, \kappa_0 = 0.28 \times 10^{-6}$		$\eta = 0.00545, \kappa_0 = 0.18 \times 10^{-6}$	
1.708	51.41	1.207	88.44
3.829	50.10	2.005	86.63
6.321	48.66	2.583	85.18
9.097	47.04	3.295	83.46
12.32	44.98	4.123	81.44
14.36	43.89	4.616	80.27
18.73	41.10	5.271	78.82
		6.168	76.84
		7.310	74.59
		8.942	71.62
		11.48	67.55

fitted with a tin condenser. The water was collected in a steam-seasoned Pyrex glass flask; precautions were taken to exclude ammonia and carbon dioxide. The water was drawn by suction, either directly into the conductance cells, or into an auxiliary flask used for making up the mixed solvents. The specific conductance of the water so obtained ranged between 0.87 and 0.35×10^{-6} mho.

Methanol for conductance measurements was purified by refluxing and drying over calcium oxide, distilling and, finally, shaking over activated alumina for a day. Distillation from the alumina gave a product whose specific conductance ranged between 0.9 and 1.8×10^{-7} mho.

C. Salts.—These were prepared and purified by conventional methods from carefully purified materials. The following salts were prepared: *n*-octadecylpyridonium iodide, m. p. $97-98^\circ$, iodine, calcd., 29.43, found, 29.35 ± 0.03 ; *n*-hexadecylpyridonium nitrate m. p. $58-59^\circ$; *n*-hexadecylpyridonium bromide m. p. $66-67^\circ$, bromine found 20.90 ± 0.02 , calcd. 20.79; *n*-octadecylpyridonium iodide m. p. $102-103^\circ$, nitrate m. p. $71-73^\circ$; bromide m. p. $74-76^\circ$, bromine found 19.33 ± 0.02 ,

calcd., 19.38; chloride m. p. 86-88°; *n*-octadecyltrimethylammonium nitrate m. p. ca. 210°.

III. Experimental Results

The conductance data for solutions of *n*-hexadecylpyridonium bromide, *n*-octadecyltrimethylammonium nitrate and *n*-octadecylpyridonium chloride in water, methanol and methanol-water mixtures are presented in Tables I, II and III, respectively. Data for *n*-octadecylpyridonium nitrate in water and *n*-octadecylpyridonium bro-

midate and nitrate in 20.01% methanol-water mixtures are given in Table IV. In the tables are given the square root of concentration (in moles per liter of solution) and the equivalent conductance, Λ . The composition of the mixed solvents, in weight per cent. of methanol, is given at the head of each table. Included in the tables are the following constants of the solvent, all at 25°: d , density; D , dielectric constant; η , viscosity (poise); and κ_0 , the specific conductance of the solvent.

TABLE II

n-OCTADECYLTRIMETHYLAMMONIUM NITRATE IN METHANOL-WATER MIXTURES AT 25°

$\sqrt{C} \times 10^3$	Λ	$\sqrt{C} \times 10^3$	Λ
5.01% Methanol		12.27% Methanol	
$d = 0.9888, D = 76.5$		$d = 0.9770, D = 73.4$	
$\eta = 0.0105, \kappa_0 = 0.75 \times 10^{-6}$		$\eta = 0.0124, \kappa_0 = 0.61 \times 10^{-6}$	
0.8605	85.50	1.107	70.12
1.102	84.99	1.283	69.96
1.430	79.78	1.496	69.74
1.782	65.57	1.763	68.99
2.362	49.44	2.131	57.82
3.115	39.01	2.458	50.83
3.737	34.09	2.961	42.50
5.370	27.18	4.152	32.29
7.259	22.37	4.889	28.84
		5.992	25.50
		7.796	22.17
15.08% Methanol ⁹		19.85% Methanol	
$d = 0.9725, D = 72.1$		$d = 0.9647, D = 70.1$	
$\eta = 0.0130, \kappa_0 = 0.72 \times 10^{-6}$		$\eta = 0.0139, \kappa_0 = 0.48 \times 10^{-6}$	
1.308	65.14	1.306	61.42
1.683	64.72	1.832	61.16
2.011	64.94	2.192	61.04
2.350	56.61	2.623	57.83
3.231	41.35	3.219	48.03
3.851	35.23	4.039	38.47
5.668	26.75	5.008	31.76
7.814	22.14	7.299	24.14
		10.40	19.95
		12.70	18.35
25.89% Methanol		34.63% Methanol	
$d = 0.9550, D = 67.4$		$d = 0.9410, D = 63.5$	
$\eta = 0.0149, \kappa_0 = 0.50 \times 10^{-6}$		$\eta = 0.0158, \kappa_0 = 0.43 \times 10^{-6}$	
2.259	56.24	2.823	51.55
2.784	56.22	3.559	51.37
3.158	55.92	3.791	51.39
3.618	52.81	4.402	51.12
4.164	47.23	5.183	49.93
4.952	40.03	5.948	46.59
7.134	28.46	7.119	33.55
8.865	24.03	9.006	32.60
		10.49	28.40
		11.38	26.54
		13.43	23.37

TABLE III

n-OCTADECYLPIRIDONIUM CHLORIDE IN METHANOL-WATER MIXTURES AT 25°

$\sqrt{C} \times 10^3$	Λ	$\sqrt{C} \times 10^3$	Λ
Water		9.9% Methanol	
$d = 0.9971, D = 78.5$		$d = 0.9805, D = 74.4$	
$\eta = 0.00895, \kappa_0 = 0.85 \times 10^{-6}$		$\eta = 0.0118, \kappa_0 = 0.81 \times 10^{-6}$	
0.9920	91.76	1.155	72.41
1.370	91.75	1.452	71.89
1.702	86.64	1.917	72.31
2.164	73.73	2.018	72.81
2.546	66.02	2.518	67.21
3.176	56.91	3.209	57.09
3.999	49.12	3.896	49.39
4.653	45.06	4.893	41.92
5.660	40.59	6.134	36.23
7.315	35.94	7.544	32.34
8.462	33.84		
14.86% Methanol		19.85% Methanol	
$d = 0.9728, D = 72.3$		$d = 0.964, D = 70.0$	
$\eta = 0.0130, \kappa_0 = 0.80 \times 10^{-6}$		$\eta = 0.0139, \kappa_0 = 0.48 \times 10^{-6}$	
1.239	64.51	1.149	60.09
1.621	64.57	1.415	60.06
1.868	65.26	1.754	60.02
2.126	66.60	2.069	60.47
2.463	66.61	2.491	61.99
2.904	64.40	2.587	61.96
3.507	56.54	3.065	61.00
4.133	50.10	3.315	59.81
4.934	43.71	3.744	56.46
6.107	37.23	4.276	52.36
7.230	33.19	4.823	47.95
		5.477	43.73
		6.107	40.13
		8.956	30.86
25.89% Methanol		34.71% Methanol	
$d = 0.9545, D = 67.4$		$d = 0.9409, D = 63.5$	
$\eta = 0.0149, \kappa_0 = 0.50 \times 10^{-6}$		$\eta = 0.0158, \kappa_0 = 0.43 \times 10^{-6}$	
1.679	53.96	3.382	48.87
2.041	54.09	3.959	48.94
2.487	55.33	4.755	49.03
3.035	55.14	5.705	48.11
3.506	55.31	6.751	45.80
4.071	54.02	8.086	42.00
5.135	49.07	10.32	36.14
6.284	43.24		
7.912	36.66		

(9) Values by P. F. Grieger, Thesis, Brown University, 1947.

TABLE IV
CONDUCTANCE OF SEVERAL SALTS IN WATER AND METHANOL-WATER MIXTURES AT 25°

$\sqrt{c} \times 10^2$	Δ	$\sqrt{c} \times 10^2$	Δ
<i>n</i> -Octadecylpyridonium Nitrate in H ₂ O; $\eta = 0.85 \times 10^{-6}$			
2.258	47.50	1.155	88.06
1.906	53.22	0.9816	89.66
1.466	70.67	.8682	90.09
<i>n</i> -Octadecylpyridonium Nitrate in 20.01% CH ₃ OH $\kappa_0 = 0.65 \times 10^{-6}$; $D = 70.0$; $\eta = 0.0139$; $d = 0.9644$			
13.50	17.16	4.513	33.18
11.37	18.33	3.491	42.43
9.803	19.61	2.787	52.97
8.267	21.43	2.300	60.54
6.823	24.09	1.832	60.88
5.723	27.26	1.502	60.74
<i>n</i> -Octadecylpyridonium Bromide in 20.01% CH ₃ OH $\kappa_0 = 0.65 \times 10^{-6}$; $D = 70.0$; $\eta = 0.0139$; $d = 0.9644$			
7.314	25.47	3.294	50.49
6.284	28.23	2.897	56.44
5.465	31.33	2.583	60.71
4.850	35.07	2.176	63.17
4.352	38.74	1.785	63.98
3.801	44.02	1.518	64.18

Not all of the measurements are recorded in the tables, but sufficient data are given to permit of accurate reproduction of the plots; the data not presented are in good agreement with those here reported; these data are shown on the plots.

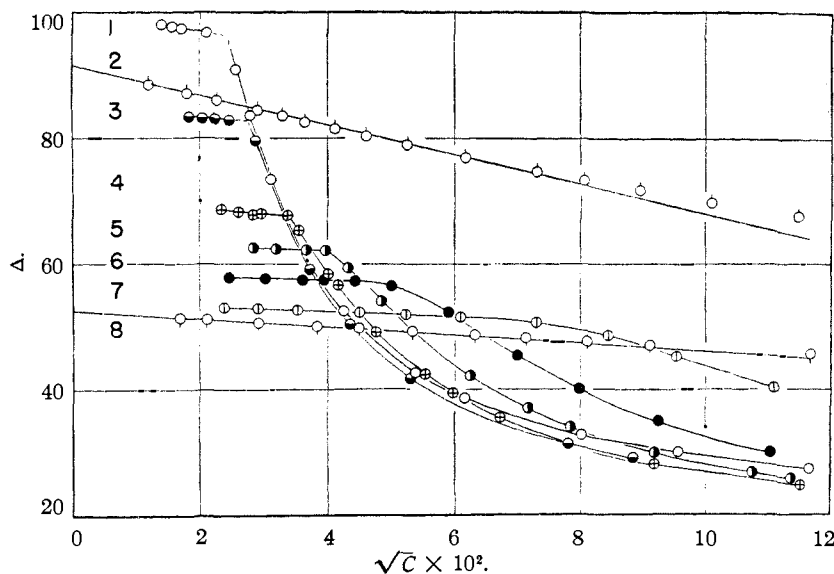


Fig. 1.—*n*-Cetylpyridonium bromide in CH₃OH-H₂O mixture: Curve 1, H₂O; 2, CH₃OH, theor. slope; 3, 6.36% CH₃OH; 4, 14.70% CH₃OH; 5, 19.91% CH₃OH; 6, 26.02% CH₃OH; 7, 35.20% CH₃OH; 8, 54.14% CH₃OH, theor. slope.

IV. Discussion

The five long chain salts measured all exhibit a behavior differing from that of ordinary salts. Four behave in water-rich methanol-water mix-

tures much as they do in water, *i. e.*, the conductance decreases with increasing concentration according to the familiar law of ordinary electrolytes but, at a certain concentration (breakpoint), the conductance begins to fall off sharply. One of the salts (octadecylpyridonium chloride), however, exhibits a markedly different behavior in that the conductance, after decreasing initially as the square root of concentration, begins to rise and passes through a maximum which is greater than the limiting conductance of the electrolyte.¹⁰ At concentrations above the critical region, the conductance falls off rapidly as in the case of the other four salts.

As may be seen from Fig. 1, octadecylpyridonium chloride in water exhibits a conductance curve similar to that of other long chain salts; the breakpoint lies at $2.54 \times 10^{-4} N$. On introducing methanol, a small, but well defined, maximum appears at 9.9% methanol. With increasing methanol content, the maximum becomes more pronounced, reaching its greatest value at 15 to 20% methanol. With further increase of methanol, the maximum becomes less pronounced and has almost disappeared at 35% methanol. The concentration at which the conductance begins to rise above the straight line changes little with increasing methanol content, but the maximum shifts toward higher salt concentrations as the content of methanol increases.

At the time that this investigation was carried out, the appearance of a maximum had not hitherto been observed at ordinary field strengths. It had, however, been observed with aqueous solutions of long chain salts at high field strengths.¹¹ More recently, maxima have been found for a number of other long chain salts in methanol-water mixtures⁹ as well as for certain salts in pure water.¹² The appearance of a maximum in the conductance curves of solutions of long chain salts has a significant bearing on our interpretation of the phenomena characteristic of these solutions. While a detailed discussion must await the presentation of further experimental material, it may be pointed out, here, that the properties of long chain salt solutions are markedly dependent on the nature of the gegenion.

The critical point of the conductance curve of solutions of hexadecyltrimethylammonium bro-

(10) Evers, Grieger and Kraus, *THIS JOURNAL*, **68**, 1137 (1946).

(11) Malsch and Hartley, *Z. physik. Chem.*, **170A**, 321 (1934).

(12) G. L. Brown, *ref. 4*.

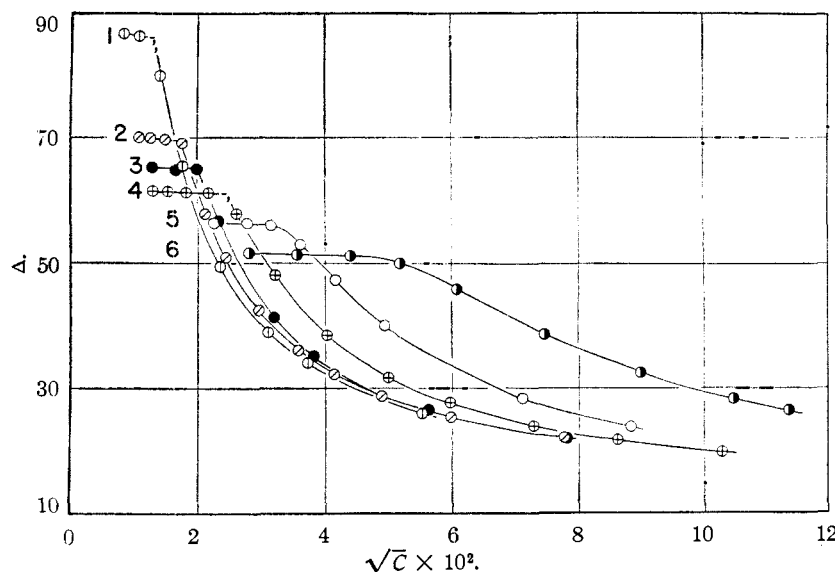


Fig. 2.—*n*-Octadecyltrimethylammonium nitrate in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixture: Curve 1, 5.01% CH_3OH ; 2, 12.27% CH_3OH ; 3, 15.08% CH_3OH ; 4, 19.85% CH_3OH ; 5, 25.89% CH_3OH ; 6, 34.63% CH_3OH .

^a Data by Grieger, Thesis, Brown University, June, 1947.

vide in methanol-water mixtures (Fig. 2) moves toward higher salt concentrations with increasing methanol content of the solvent mixture. As far as 20% methanol, the break appears sharp, but at 26 and 35% methanol, the tangent to the curve shows no discontinuity. For 54% methanol, the conductance is a linear function of \sqrt{C} as far as $2 \times 10^{-2} N$. The measured conductances are given within the experimental error by the equation: $\Lambda = 52.4-59.5 \sqrt{C}$. The slope of the curve is approximately 7% below the Onsager theoretical value. It is surprising to find the linear relation holding to such high concentrations; probably this is due to compensating factors.

In pure methanol the conductance for hexadecyltrimethylammonium bromide is reproduced within the experimental error by the equation: $\Lambda = 91.53-245 \sqrt{C}$. The slope is 7% greater than the theoretical and, at higher concentrations, the experimental values deviate toward higher conductances. Such deviations are common in aqueous solutions of ordinary salts. The fact that a long chain salt deviates in this direction in methanol appears to be good evidence that such salts are normal electrolytes in this solvent.

Although limiting conductances cannot be de-

termined with precision from the present measurements because of the high conductance of the solvent mixtures, reasonably reliable values may be approximated. The conductance viscosity product, $\Lambda_0\eta$, for hexadecyltrimethylammonium bromide, beginning with a value of 0.898 in pure water, passes through a maximum of 0.917 at approximately 6% methanol and thereafter diminishes regularly to a value of 0.499 for pure methanol. This behavior is similar to that of the lithium ion in methanol-water mixtures as determined by Longworth and MacInnes,¹³ who found a maximum near 16% methanol. Similar effects have been observed for solutions of potassium and sodium iodides and sodium and lithium chlorides

in ethanol-water mixtures by Connell, Hamilton and Butler,¹⁴ the maximum lying in the neighborhood of 6 to 10% ethanol (by weight). The occurrence of this maximum in the case of a long chain salt serves as supporting evidence for the

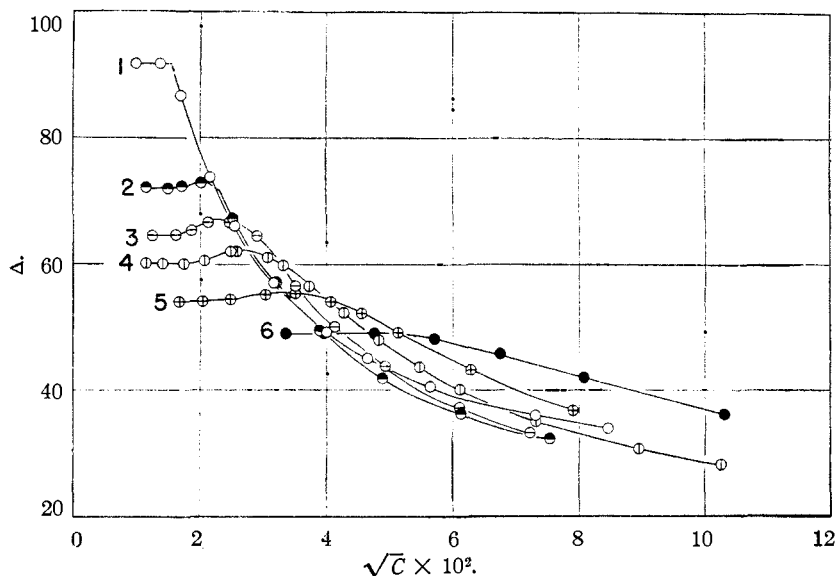


Fig. 3.—*n*-Octadecylpyridonium chloride in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixture: Curve 1, H_2O ; 2, 9.90% CH_3OH ; 3, 14.86% CH_3OH ; 4, 19.86% CH_3OH ; 5, 25.89% CH_3OH ; 6, 34.71% CH_3OH .

view that such salts are normal electrolytes at low concentrations and below the breakpoint.

One other characteristic of the conductance

(13) Longworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).
 (14) Connell, Hamilton and Butler, *Proc. Roy. Soc. (London)* **147A**, 418 (1934).

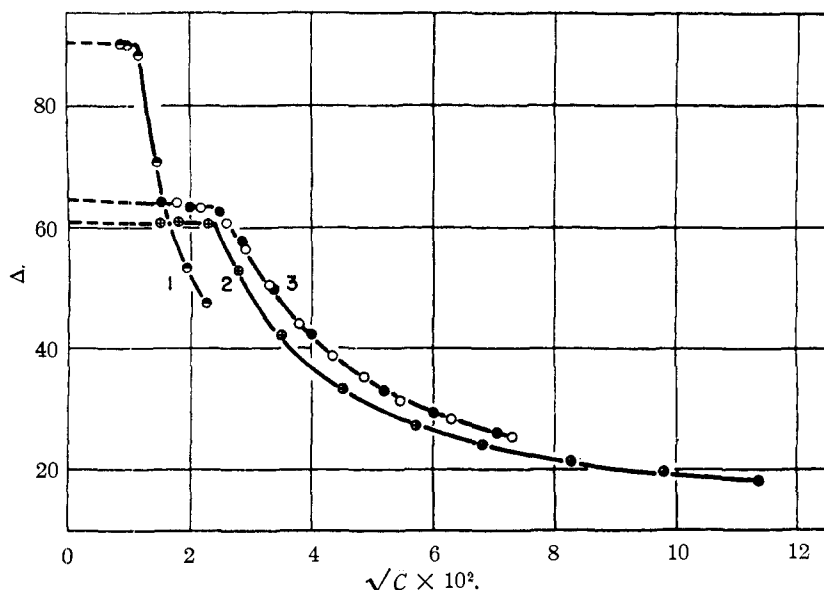


Fig. 4.—Conductance curves for salts in water and in methanol mixtures: Curve 1, octadecylpyridonium nitrate in H_2O ; 2, octadecylpyridonium nitrate in 20% CH_3OH ; 3, octadecylpyridonium bromide in 20% CH_3OH .

curves of hexadecylpyridonium bromide in methanol-water mixtures may be pointed out. As the content of methanol is increased up to 14.7%, the breakpoint lies on the curve for the same substance in water at concentrations above the breakpoint. The curves for these solutions at higher concentrations lie close together and parallel one another fairly closely. For mixtures containing more than 14.7% methanol, the decrease in conductance with increasing salt concentration diminishes and, at 35.2% methanol, the conductance decrease is small and appears only at relatively high concentrations.

The curves for octadecyltrimethylammonium nitrate (Fig. 3), although the breakpoints come at much lower concentrations, parallel those of hexadecylpyridonium bromide rather closely. The curves for 35% methanol are strikingly similar for the two salts, both as to form and conductance values. In this connection, it is of interest to note that for 35% methanol, the curve for octadecylpyridonium chloride closely resembles those for the two salts discussed above.

On the basis of the considerations advanced above, it appears that the presence of methanol modifies the conductance of different long chain salts in much the same manner, irrespective of chain length or of gegenion. On the other hand, the breakpoint concentration and the appearance of a maximum are greatly dependent on the nature of the gegenion. Thus, the breakpoint for octadecylpyridonium nitrate appears at $1.28 \times$

$10^{-4} N$ (Fig. 4) while that of the chloride appears at 2.54×10^{-4} . The gegenion not only has an influence on the form of the conductance curve (maximum or breakpoint), it also has a marked influence on the concentration at which salts of a given long chain cation begin to diverge from the theoretical relations that apply in the case of dilute solutions of ordinary salts. For mixtures containing approximately 20% methanol, the breakpoint for different octadecyl salts occurs at approximately the same concentration, $6 \times 10^{-4} N$. Excepting for the maximum, individual differences tend to disappear, with increasing methanol content.

IV. Summary

1. The conductance of hexadecylpyridonium bromide, octadecyltrimethylammonium nitrate and octadecylpyridonium nitrate chloride and bromide has been measured in methanol-water mixtures at 25° .

2. With the exception of octadecylpyridonium bromide, all salts have been measured in pure water and all show a normal breakpoint in that solvent.

3. All salts measured, with the exception of octadecylpyridonium chloride, show breakpoints in mixtures of higher methanol content.

4. The phenomena that characterize the breakpoint become less pronounced with increasing methanol content of the solvent.

5. The properties that distinguish solutions of long chain salts from those of normal electrolytes appear to disappear in the neighborhood of 50% methanol or somewhat above this value.

6. The conductance curve for hexadecylpyridonium bromide in a solvent of 54% methanol content, as well as in pure methanol, closely approximates the theoretical limiting slope.

7. The behavior of octadecylpyridonium chloride differs from that of the other salts studied in that a maximum appears somewhere below 10% methanol. The maximum effect is greatest at 15 to 20% methanol and has almost disappeared at 35% methanol. The maximum moves toward higher concentration with increasing methanol content of the solvent.

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