[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Bolaform Electrolytes.[1] II. Conductance of 1,3-, 1,4- and 1,5-Di-(trimethylammonium)-polymethylene Halides in Water and in Methanol[2]

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Conductance at 25° in water and in methanol of the following salts have been measured: $Br'(Me_3N^+(CH_2)_3N^+Me_3)Br'$, $(Me_3N^+(CH_2)_3N^+Me_3)I'$, $I'(Me_3N^+(CH_2)_4N^+Me_3)I'$ and $I'(Me_3N^+(CH_2)_5N^+Me_3)I'$. Analysis of the conductance curves by the method of Fuoss and Edelson shows that there is some association ($k_2 \approx 0.1$) of *one* halide ion to the doubly charged cation in water, and considerable association ($k_2 \approx 0.001$) in methanol. The dependence of dissociation constant on chain length suggests curled configurations in the associated ion pairs ${}^+B^+A'$.

Introduction

In the first paper of this series,[3] we presented experimental data on a salt whose cation contained two quaternary ammonium ions connected by a chain of ten atoms. This salt was somewhat unstable in aqueous solution due to the presence of ester linkages in the cation; we therefore decided to investigate cations of the general formula

$$Me_3N^+(CH_2)_nN^+Me_3 \qquad (1)$$

in which no hydrolyzable bond is present. In this paper, conductance data for the trimethylene dibromide and diiodide and for the tetra- and pentamethylene diiodides in water and in methanol at 25° are presented. For convenience, we shall refer to these as the C3, C4 and C5 dihalides. The salts all show appreciable association of one anion to the divalent cation in aqueous solution, and as might be expected, a considerably greater association in methanol. The extrapolation method described in our first paper was used to obtain values of the limiting conductance Λ_0 and the dissociation constant k_2 which describes the equilibrium

$$AB^+ \rightleftarrows A' + {}^+B^+ \qquad (2)$$

Experimental methods were essentially as already described.[3] Symbols in the discussion have the same meaning as before[3] and need not all be redefined here.

Experimental

1,3-Di-(trimethylammonium)-trimethylene diiodide was prepared by adding methyl iodide to tetramethyltrimethylenediamine[4]: 11.17 g. (0.086 mole) of the latter was dissolved in 90 ml. of 95% alcohol and 24.9 g. (0.176 mole) of methyl iodide was added slowly, with occasional cooling. On standing 2 hr., the mixture set solid. The mass was broken up and filtered; 35 g. of white crystals was obtained. Recrystallization from 90 g. of alcohol gave 31.5 g. of final product; dec. 345–350°; iodide (potentiometric) 61.26, 61.30, 61.23%; theoretical 61.29%.

1,3-Di-(trimethylammonium)-trimethylene dibromide was prepared by adding trimethylamine to 1,3-dibromopropane: 12.5 g. (0.062 mole) of the latter and 55 g. of 25% trimethylamine (0.232 mole) in methanol were refluxed for 80 min. and then the solution was concentrated to one-quarter the starting volume. On cooling to room temperature, 16.0 g. of salt separated. Addition of petroleum ether to the mother liquor precipitated an additional 3.9 g. The salt was washed with ethanol and petroleum ether, and recrystallized from ethanol (2.6 cc./g.). Solubilities were found as follows: in methanol, 1.10 g./cc. at 20°, 1.58 at 40°, 2.32 at 60°; in 95% ethanol, 0.05 g./cc. at 40°, 0.15 at 50°, 0.31 at 60°, 0.52 at 70°, 0.71 at 78°. Bromide was determined potentiometrically; first crop, 49.88, 49.90%; recrystallized material, 49.84, 49.80%; theoretical, 49.98%.

1,4-Di-(trimethylammonium)-tetramethylene diiodide was prepared by refluxing 61.1 g. of 25% trimethylamine (0.255 mole) in methanol with 19.5 g. (0.062 mole) of 1,4-diiodobutane for 5 hr. (The latter was prepared from 1,4-dichlorobutane and sodium iodide in acetone; b.p. 82–84° at 2.4 mm.) The solution was concentrated to half-volume; on standing at room temperature, salt crystallized out. After washing with chilled absolute ethanol, it was recrystallized from 97.0% ethanol (12.0 cc./g.). Solubility in absolute ethanol; 0.017 g./cc. at 35°, 0.032 at 45°, 0.064 at 55°, 0.091 at 60°. Analyses both by gravimetric and potentiometric methods were about 1% low until excess sodium sulfate (*ca.* 10% in the solution) was added; this suppressed adsorption of iodide ion from solution onto the precipitated silver iodide. Iodide found potentiometrically: 59.19, 59.19, 59.20, 59.11%; theoretical, 59.30%. The salt begins to decompose at 175° and liquefies completely by 190°.

1,5-Di-(trimethylammonium)-pentamethylene diiodide was prepared by refluxing 33.0 g. (0.102 mole) of 1,5-diiodopentane (from 1,5-dichloropentane and sodium iodide in acetone; b.p. 99–100° at 2.4 mm.) with 99 g. of 25% trimethylamine (0.424 mole) in methanol for 5 hr. On concentration to half-volume and chilling, salt crystallized out. It was twice recrystallized from 93.8% ethanol (7.4 cc./g.). Potentiometric iodide: 57.18, 57.17; theoretical, 57.42%.

Methanol was purified over aluminum amalgam,[5] followed by a distillation from freshly ignited calcium oxide. (Without the lime treatment, solutions of the iodides in methanol become yellow on standing several hours.) Specific conductance, 1.5 × 10^{-7} mho; density, 0.78659 at 25.00°.

Results

The conductance data are given in Tables I and II. Concentrations c are given as equivalents of halide per liter of solution and Λ is 1000 times the corrected specific conductance over c. Slight (<0.1%) polarization errors were eliminated by extrapolation to infinite frequency.[6] Different series are indicated by superscript italics, *a*, *b*, etc. Both concentration and dilution runs were made. All solutions were made up by weight (corrected to vacuum), and calculated to a volume basis by means of the densities given in Table III where m denotes moles salt/kg. solution; the density was assumed linear in concentration.

Discussion

The conventional conductance curves are shown for the four salts in Figs. 1 (water) and 2 (methanol). The theoretical limiting slopes for 2–1 electrolytes are drawn as dotted lines. In the aqueous solutions, an inflection region appears, but the approach to the limiting tangent is visible

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(1) Office of Naval Research, Project NR 054-002; Paper No. 28.

(2) This paper is based on part of a thesis submitted by Victor F. H. Chu to the Graduate School of Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950. E. I. du Pont de Nemours and Company, Photoproducts Research Laboratory, Parlin, N. J.

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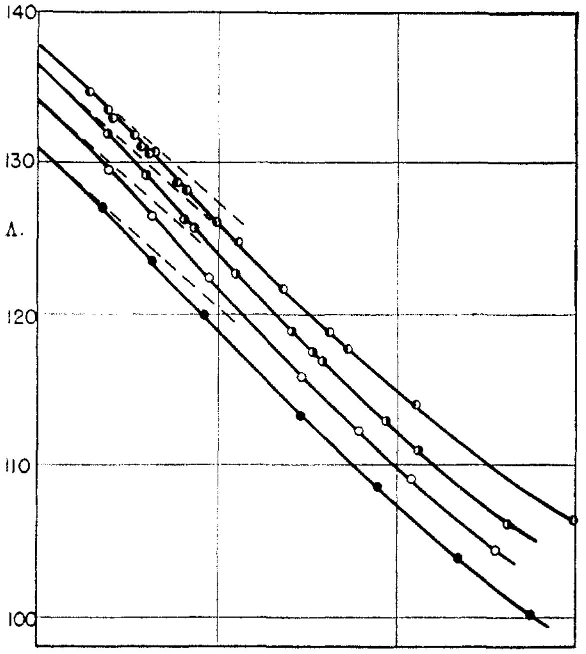

Fig. 1.—Conductance curves in water: left-black, C3.Br'₂; right-black, C3.I'₂; open circles, C4.I'₂; solid circles, C5.I'₂.

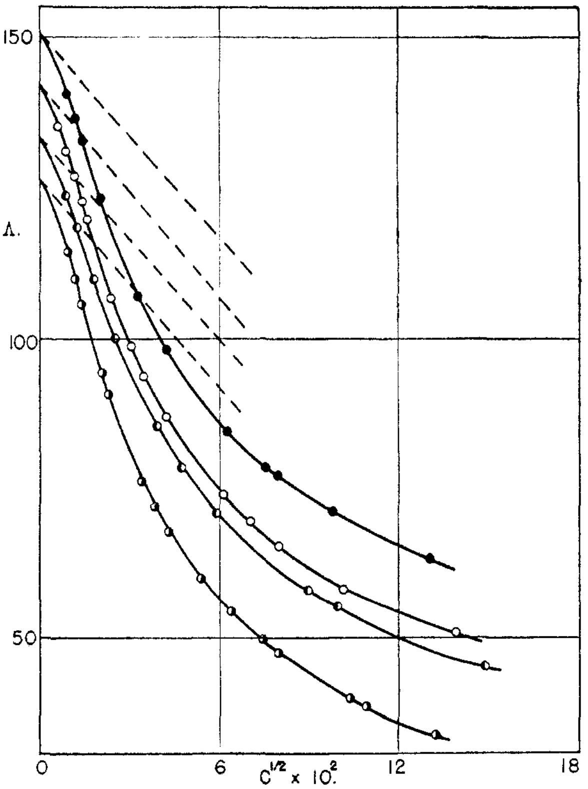

Fig. 2.—Conductance curves in methanol: left-black, C3.Br'₂; right black, (Λ − 15) for C3.I'₂; open circles, C4.I'₂; solid circles, (Λ + 10) for C5.I'₂.

in the accessible concentration range. Some association is therefore clearly indicated. In methanol, however, the Λ-c curves are much steeper; as might be expected from the lower dielectric constant as compared to water, association is greater and approach to the limiting tangent occurs only at high dilutions.

TABLE I

CONDUCTANCES OF $Me_3N^+ (CH_2)_nN^+Me_3$ DIHALIDES IN WATER AT 25.00°

$c \times 10^3$	Λ	$c \times 10^3$	Λ	$c \times 10^3$	Λ
C3 dibromide		C4 diiodide		7.250^c	118.93
0.6523^a	133.00	0.6141^a	129.59	8.515^b	117.52
1.2224^a	131.03	1.5220^a	126.55	9.064^a	116.93
1.4313^c	130.64	3.3701^a	122.45	13.559^c	112.89
2.2082^a	128.61	7.897^b	115.99	16.270^b	110.91
2.5312^c	128.15	11.533^a	112.33	24.684^b	106.07
3.5817^a	126.04	15.716^b	109.11	C5 diiodide	
3.6091^c	126.23	23.563^b	104.37	0.4954^a	127.02
4.535^c	124.73	C3 diiodide		1.5384^a	123.44
6.807^b	121.64	0.5856^a	131.96	3.1496^a	120.02
9.589^b	118.79	1.3638^a	129.23	7.827^b	113.38
10.804^a	117.67	2.4773^c	126.34	13.049^a	108.61
16.029^b	113.94	2.7984^a	125.76	20.061^b	103.89
32.170^b	106.27	[4.4551^c	122.68	27.391^b	100.16

TABLE II

CONDUCTANCES OF $Me_3N^+(CH_2)_nN^+Me_3$ DIHALIDES IN METHANOL AT 25.00°

$c \times 10^3$	Λ	$c \times 10^3$	Λ	$c \times 10^3$	Λ
C3 dibromide		1.0195^b	97.85	4.188^d	69.37
$0.07825,^a$	123.66	1.2390^c	93.88	5.652^a	64.61
$.15561,^a$	118.39	1.7943^c	87.10	6.467^d	62.42
$.3289^a$	109.89	3.7354^d	74.14	10.975^d	54.60
$.6621^b$	100.01	5.045^b	69.18	12.022^c	53.37
$1.5362,^b$	85.41	6.469^c	65.26	17.796^d	48.22
2.2700^b	78.67	10.393^d	58.14	C5 diiodide	
3.5361^c	70.96	19.386^d	50.13	0.08822^a	130.43
8.073^b	58.12	C3 diiodide		$.14812^a$	126.55
9.960^c	55.23	0.09101^a	129.40	$.20886^a$	122.80
22.141^c	45.29	$.14765^a$	124.86	$.4355^a$	113.44
C4 diiodide		$.21330^a$	120.54	$.5459^b$	109.13
0.04771^a	135.00	$.4705^a$	109.27	1.1186^c	97.03
$.09643^a$	130.88	$.5622^b$	105.71	1.8028^b	88.46
$.15351^a$	126.87	1.2005^b	91.27	3.968^c	74.72
$.22398,^a$	122.72	1.5215^c	87.05	6.329^b	67.30
$.28167^a$	119.78	1.9134^b	82.84	9.618^c	61.01
$.5966^c$	106.79	2.9808^c	75.11	16.995^c	53.37

TABLE III

DENSITIES OF SOLUTIONS AT 25.00°

Salt	Water		Methanol	
	$m \times 10^3$		$m \times 10^3$	
C3. Br'₂	5.154	0.99889	4.500	0.78855
C3. I'₂	5.104	.99928	4.670	.78892
C4. I'₂	5.047	.99928	4.493	.78855
C5. I'₂	6.058	.99940	4.762	.78886

If we assume that the deviations from the limiting law are due to association of halide ions to the divalent cation according to Eq. (2), the conductance and dissociation equations can be combined to give

$$\Lambda' = \Lambda_0 - x/k_2 \Lambda_0 \qquad (3)$$

where $\Lambda' = \gamma_1\Lambda_0$ and γ_1 is the ratio of the concentration of free halide ions to the stoichiometric halogen concentration c. The variable Λ' contains an estimate of the effects of interionic forces on the mobilities of the three species (A', AB^+ and B^{++}) of ions present. The variable x is defined as

$$x = c'\Lambda'(\Lambda' - \Lambda_0/2) \qquad (4)$$

where c' is $f_B c$ and f_B is the activity coefficient of the divalent cation. In our previous paper,[3] we calculated f_B by the limiting equation ($-\log f_B =$

$9.81\sqrt{c}$); here we have introduced a second approximation

$$-\log f_B = 9.81[(4\gamma_1 - 1)c/3]^{1/2} \qquad (5)$$

to allow for association in the concentration appearing in the activity correction. A similar correction was likewise made in the mobility terms in $\sqrt{\ }$. Data for several salts were also computed with the inclusion of the $(1 + \kappa a)^{-1}$ term in Eq. (5); in our present concentration range, its effect was slight, as shown by the insensitivity of the results to the *a*-value chosen; the simpler expression (5) was therefore used.

Equation (3) is a simple linear equation in Λ' and x, with intercept Λ_0 at $x = 0$ and slope $1/k_2\Lambda_0$. It will be noted, however, that Λ_0 appears in the definition of x in Eq. (4); a value for Λ_0 is also needed to compute the interionic correction terms required to evaluate Λ' and x. This apparent cycle of ambiguity is eliminated by a process of successive approximations. A free-hand extrapolation of the Λ–$\sqrt{c}$ curve (which gives too high a Λ_0 if the inflection region is extrapolated linearly) gives a preliminary working value (zero approximation) of Λ_0 which is used to start the calculation. The resulting Λ'–x plot extrapolates to quite nearly the correct value of Λ_0, because the equations for Λ' and x are so contrived that they are not very sensitive to the value of Λ_0 used. The value of Λ_0 obtained from the first Λ'–x plot is then used to recompute the various functions and then a final extrapolation is made. When the data cover the inflection range of the Λ–$\sqrt{c}$ curve, one cycle of approximations as described above is sufficient: repetition does not change the value of Λ_0 within the experimental error of determining Λ.

Final extrapolation curves for the four salts investigated are shown in Figs. 3 (water) and 4 (methanol). To simplify the figures, several of the ordinate scales are displaced, as given in the captions of the figures. For the aqueous systems, the points are linear, well within 0.1%. Some apparently systematic concavity appears at higher concentrations in the methanol plots, but the approach to the linearity at low concentrations is unmistakable, and permits a reliable extrapolation for Λ_0 and k_2.

The results of the extrapolations are summarized in Table IV. Not many comparisons with previous data can be made. The difference between bromide and iodide conductances in water from Table IV (C3 salts) is 1.37, which agrees well with

TABLE IV

CONSTANTS FOR SALTS IN WATER AND IN METHANOL

System	Λ_0	k_2	$\lambda(+)$
$C3.Br'_2$–H_2O	137.89	0.16	59.6
$C3.I'_2$–H_2O	136.52	.125	59.7
$C4.I'_2$–H_2O	134.20	.13	57.4
$C5.I'_2$–H_2O	131.06	.135	54.3
$C3.Br'_2$–MeOH	133.05	.00104	(76.6)
$C3.I'_2$–MeOH	141.3	.00081	(80.3)
$C4.I'_2$–MeOH	142.05	.00103	(81.1)
$C5.I'_2$–MeOH	140.05	.00108	(79.1)

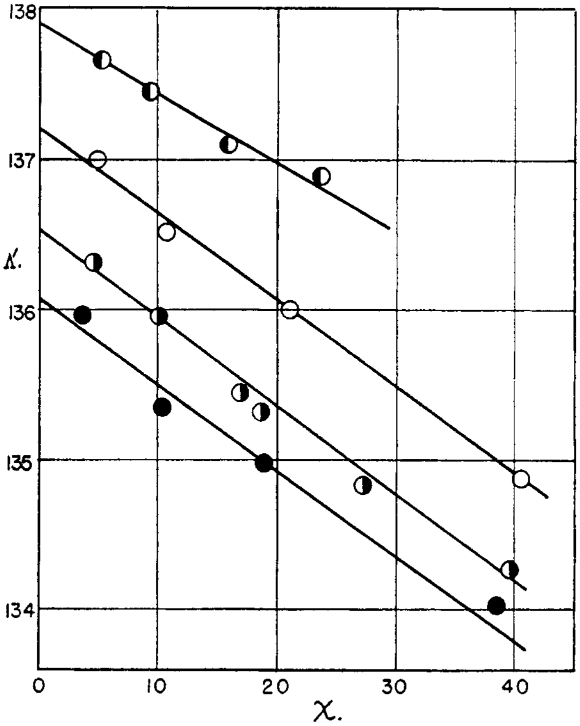

Fig. 3.—Extrapolation plots in water: left black, $C3.Br'_2$; right black, $C3.I'_2$; open circles, (Λ' + 3) for $C4.I'_2$; solid circles, (Λ' + 5) for $C5.I'_2$.

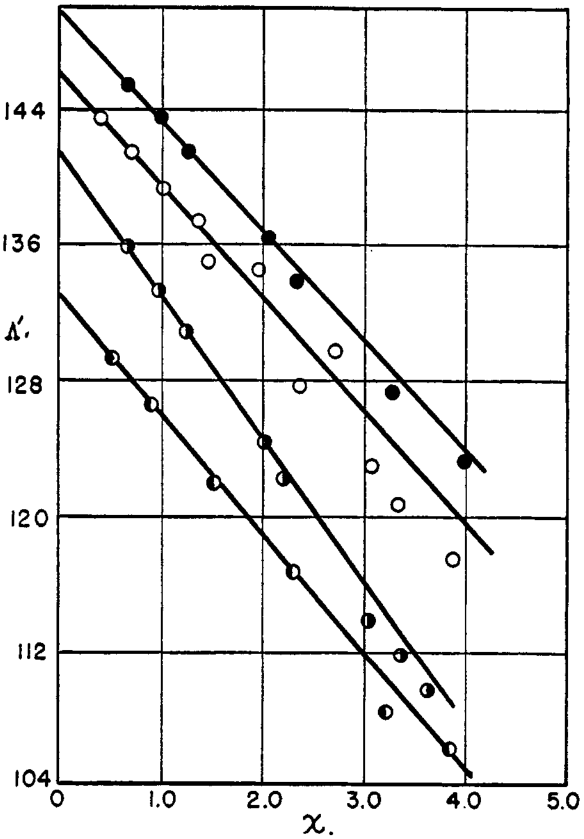

Fig. 4.—Extrapolation plots in methanol: left-black, $C3.Br'_2$; right-black, $C3.I'_2$; open circles, (Λ' + 4) for $C4.I'_2$; solid circles, (Λ' + 9) for $C5.I'_2$.

the accepted difference[7] of 1.5. In methanol, we find 8.25 for this difference. Data for tetramethylammonium bromide and iodide in methanol[8] were extrapolated[9] to give, respectively, Λ_0 = 125.33 and 131.77; similarly, data for tetraethylammonium bromide and iodide in methanol[10] extrapolated to 117.00 and 123.73. The differences, 6.44 and 6.73, are somewhat smaller than our value. The English authors[10,11] give for single ion conductances in methanol $\lambda(\text{Br}') = 55.5$ and $\lambda(\text{I}') = 61.0$, with a difference of 5.5; these values in turn are based on (1) a determination of the transference number of hydrogen ion[12] obtained by e.m.f. measurements on concentration cells of HCl (0.0045 to 0.155 N) in methanol, and (2) Wynne-Jones' value[13] of the limiting mobility of HCl in methanol. In our calculations for Figs. 3 and 4, we used the above values of the single ion conductances, because no others are available. The discrepancies, however, are greater than the estimated experimental errors and redetermination of the single ion conductances seems advisable, especially in view of the rather high range of concentration used by Nonhebel. The method of Fowler and Kraus[14] is probably more reliable than the e. m. f. method in this range of dielectric constant. The parentheses in Table IV indicate that the cation conductances given there are tentative.

The sequence of limiting conductances in water is as expected: decreasing with increasing length of the methylene chain. The value for the C_3 iodide in methanol is, however, puzzling: one would expect Λ_0 to be about 144, based on the results for the C4 and C5 salts, but then the bromide-iodide difference would be in even poorer agreement with the values obtained from the 1-1 tetraalkylammonium salts.[9,10] We plan to measure the nitrates in an effort to clarify this point. Some interesting problems in solvation are suggested by the double reversal in going from water to methanol: the halide ions become slower and the bolaform ions become faster by about the same amount, so that the net change in total conductance is rather small. This observation recalls the hazards of applying Walden's rule to total (rather than ionic) conductances.

It is premature to say much about the k_2 values. The fact that the C3, C4 and C5 bromides have values which differ so little in a given solvent suggests, however, that in the associated pair $^+\text{B}^+\text{A}'$ the chain is probably curled up under the attractive field of the anion, because an extended configuration would lead to a increase of k_2 with increasing chain length, corresponding to diminished attraction from the unpaired charge on the cation. The fact that a bolaform electrolyte with ten atoms[3] between charges has $k_2 = 0.0045$ is methanol suggests that the entropy loss involved in cyclizing a long chain outweighs the energy gain; in other words, k_2 will increase with increasing chain length, but less rapidly than would be predicted on the basis of the extended configuration. In the limit of very long chains, k_2 should approach then the value of one quarter the constant for 1-1 salts (the four is the familiar[15] statistical factor), and become independent of chain length. Further work on other bolaform electrolytes is in progress.

NEW HAVEN, CONN. RECEIVED AUGUST 21, 1950

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