TABLE I

ELECTROLYSIS OF ALUMINUM HALIDE–IODINE HALIDE SOLUTIONS IN ACETONITRILE

	Run	Cell compartment molalities Cathode	Middle	Anode	Av.	Original soln.
$AlCl_3$–ICl soln.	I	0.0689	0.0648	0.0557	0.0631	0.0626
(Al anal.)	II	.0688	.0668	.0586	.0647	.0652
	III	.0708	.0672	.0593	.0658	.0663
(I_2 and Cl_2	IV I_2	.1744	.1806	.2253	.1934	.1902
anal.)	Cl_2	.3829	.4090	.4779	.4197	.4248
	V I_2	.1692	.1784	.2124	.1867	.1900
	Cl_2	.3833	.4054	.4817	.4235	.4229
$AlBr_3$–IBr	I	.0746	.0701	.0624	.0690	.0687
soln. (Al anal.)	II	.0752	.0676	.0572	.0666	.0666
$AlCl_3$–IBr	I	.0688	.0657	.0557	.0634	.0634
soln. (Al anal.)	II	.0866	.0840	.0730	.0812	.0813
$AlBr_3$–ICl	I	.0709	.0684	.0581	.0657	.0658
soln. (Al anal.)	II	.0396	.0375	.0306	.0359	.0360

equal to 1:2, which is that for the ICl_2^- ion. The data given in Table I are typical of a number of runs made in the investigation. The results were reproducible and no change in the direction of ionic migration was observed upon varying either the total concentration or the relative concentration of the halides, or both.

In general, the spectrophotometric and the electrolysis studies essentially yield the same results. In acetonitrile solutions containing an iodine halide and an aluminum halide, the former reacts with a halide ion produced by the dissociation of aluminum halide. The literature is rather vague on the nature of the dissociation of aluminum halides in non-aqueous solvents. Electrolysis studies in such solvents as ethyl bromide, benzene and nitrobenzene indicate that aluminum bromide preferentially exists in the anion form $AlBr_4^-$ or $Al_2Br_7^-$,[13] although recently Fairbrother and Scott report[14] that in ethyl bromide solutions there is a net transport of aluminum to the cathode and bromine to the anode. They suggest that the conducting species are $AlBr_4^-$ and $EtBrAlBr_2^+$. Also a study on the hydrogen bromide–aluminum bromide–benzene system failed to give any evidence for the existence of $AlBr_4^-$ ion.[15]

The results of this investigation do not exclude the possibility of AlX_4^- ion being present in acetonitrile solutions of aluminum halides. On the other hand, the formation of polyhalide ions with iodine monochloride or iodine bromide indicates that such solutions must contain appreciable amounts of free halide ions. This is substantiated by the observation that upon addition of silver perchlorate solution in acetonitrile to aluminum chloride or aluminum bromide solution in the same solvent, quantitative precipitation of silver halide was obtained. That similar type of dissociation occurs in acetone solutions has been pointed out by Ushakov.[16]

It seems, therefore, permissible to conclude that aluminum halide in acetonitrile is strongly solvated (as the $AlCl_3{\cdot}2CH_3CN$ compound) and, at least partially undergoes a dissociation according to

$$AlCl_3{\cdot}nCH_3CN \rightleftarrows AlCl_m{\cdot}nCH_3CN^{+(3-m)} + (3-m)Cl^-$$

with m = 2, 1 or 0. The extent of this dissociation need not be great to give practically quantitatively the corresponding polyhalide ion upon addition of an iodine halide, since the formation constants of the polyhalide ions are of the order of magnitude of 10^7.[17]

Acknowledgment.—The authors are indebted to the Research Corporation for the support of this work and to Dr. W. E. Bennett and Mr. W. A. Deskin of this Laboratory for the preparation of pure aluminum bromide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. IX. Electrical Conductance Study of Higher Polyiodide Complex Ions in Acetonitrile Solutions[1,2]

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Electrical conductance studies on the tetramethylammonium and the tetrapropylammonium polyiodides in acetonitrile solutions show that the heptaiodide ion is relatively stable in solutions which are $\geq 10^{-2}$ *M*. Below this concentration, it begins to dissociate into the pentaiodide and iodine, and this process is virtually complete in 9×10^{-4} *M* solutions. The pentaiodide in its turn is unstable in solutions which are $\leq 2 \times 10^{-4}$ *M*. The lower limit for the dissociation constant of the heptaiodide ion is calculated to be 7.0×10^{-3}, while that for the pentaiodide is 2.0×10^{-3}.

Solid polyiodide compounds containing such ions as I_5^-, I_7^- and I_9^-, mainly in combination with large cations such as tetraalkylammoniates, have been known for a considerable time.[3] However, the question of their existence in solutions still has not been completely settled. The arguments for the existence of the polyiodides higher than the triiodide, in various solvents, mainly come from some early studies of the distribution coefficients of iodine between a non-polar solvent and an aqueous solution of potassium or some other iodide.[4] On

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(1) Abstracted in part from the Ph.D. Theses of Norman E. Skelly andof Ralph H. Rygg, Graduate College, State University of Iowa.

(2) Presented before the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April 1955.

(3) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 453.

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the other hand recent X-ray crystallographic work on the tetraalkylammonium pentaiodide,[5] heptaiodide[6] and enneaiodide[7] seems to cast considerable doubt on the possibility of existence of the last two ions in solutions. Spectrophotometric study of the tetramethylammonium triiodide, pentaiodide and enneaiodide in ethylene dichloride solutions[8] have shown that the absorption spectra of the two higher iodides in concentration approximately 10^{-5} M are identical to that of the triiodide ion plus that of the excess of free iodine.

Since any significant formation of large polyiodide ions in the triiodide–iodine solutions should markedly affect the electrical conductance of these solutions, it was thought that such a study might add some useful information as to the existence and stability of these higher polyiodides.

Experimental Part

Apparatus.—The conductivity apparatus and the conditions of measurements have been described in a previous communication.[9] A total of five conductance cells of the Jones–Bollinger type,[10] with cell constants varying from 3.600 to 0.0491 were used. The cell constants were determined with known potassium chloride solutions using specific conductance values given by Shedlovsky.[11] Each cell was calibrated with several solutions of varying concentration to obtain a correction for an observed slight Parker effect. The cell calibrations and all of the subsequent measurements were made at 25 ± 0.01° and with unplatinized electrodes. Resistance measurements were reproducible to within 0.3%.

Viscosity Measurements.—Viscosity measurements were made at 25.0 ± 0.10° using an Ostwald–Fenske type viscosimeter and a Lipkin pycnometer.

Spectrophotometric Measurements.—All spectrophotometric measurements were made on a Cary recording spectrophotometer, Model 11, with silica cells of 1.00 ± 0.01 cm. path length and at room temperature of approximately 25°.

Reagents.—Quaternary ammonium iodides were obtained from the Eastman Kodak Company and were purified by recrystallization from alcohol–ether mixtures. The melting points of recrystallized products agreed with those reported in the literature. Gravimetric analysis for iodine gave quantitative results within the limits of experimental error.

Polyiodides used in this investigation were prepared by the method of Chattaway and Hoyle.[12] The tetrapropylammonium triiodide has a melting point of 98.5° (reported[12] at 97°) and iodometric analysis yielded an iodometric equivalent of 284.0 (theoretical, 283.6). The tetrapropylammonium pentaiodide apparently has two crystalline forms, one, dark green needles, and the other, metallic green platelets, as reported previously. Both forms had a melting point of 82° (reported as 82°) and an iodometric equivalent of 206.4 (theoretical, 205.3). The tetrapropylammonium heptaiodide gave a melting point of 84–85° (reported as 85°) and its iodometric equivalent was 185.1 (theoretical 179.1).

The tetramethylammonium triiodide had a melting point of 117.8° (reported as 118°) and an iodometric equivalent of 228.5 (theoretical, 227.5). The tetrapropylammonium pentaiodide had a melting point of 132° (reported 132°), and an iodometric equivalent of 177.9 (theoretical, 177.1).

The iodine used in the solution preparation was the "Baker analyzed reagent grade" purified by sublimation from barium oxide and potassium iodide.

The acetonitrile was purified in the manner previously described.[9] The specific conductance of the solvent used in the present measurements varied from 0.6 to 1.7 × 10^{-7} ohm^{-1} cm.$^{-1}$.

Baker purified nitrobenzene was further purified by the method of Witschonke and Kraus.[13] At a pressure of about two mm. the product was distilled at 65° and its specific conductance varied from 1 to 3 × 10^{-9} ohm^{-1} cm.$^{-1}$.

Solutions.—Solutions from 10^{-2} to 10^{-3} molar were prepared by dissolving a weighed amount of electrolyte in a known volume of solvent. Solutions of lower concentrations were prepared by dilution, either by the volume dilution method or on a weight basis using a weighing buret. These solutions were all made to the desired volume at 25.0°. All glassware was calibrated with conductivity water at this temperature.

The conductance measurements were made within a six-hour period after the preparation of the solutions. The latter were found to be stable for, at least, a 24-hour period, with the exception of those containing free iodine.

The specific conductance of the solvent was always less than 1% of the total specific conductance of the most dilute solutions.

Results and Discussion

The equivalent conductance values in acetonitrile solutions for the tetramethylammonium iodide, triiodide and pentaiodide, as well as for the tetrapropylammonium iodide, triiodide, pentaiodide and heptaiodide are given in Table I. For comparison purposes, results are also given for the tetramethylammonium pentaiodide solutions to which an equimolar amount of iodine has been added so as to give a composition equivalent to I_7^- ion.

TABLE I

EQUIVALENT CONDUCTANCES OF THE TETRAMETHYL- AND TETRAPROPYLAMMONIUM POLYIODIDES IN ACETONITRILE AT 25.0°

Me_4NI $C \times 10^5$	Λ	Me_4NI_3 $C \times 10^5$	Λ	Me_4NI_5 $C \times 10^5$	Λ	Me_4NI_5 + I_2 $C \times 10^5$	Λ
....	...	1000	159.0	942.6	155.9	1000.0	152.8
497.2	161.3	500.0	167.1	480.3	164.5	949.9	153.4
250.6	171.6	250.0	172.5	188.4	174.3	492.5	162.8
121.6	178.9	114.2	178.5	108.6	178.2	472.2	164.2
70.56	183.2	70.13	181.5	63.51	180.4	275.7	169.0
53.85	184.3	60.06	182.0	14.14	187.0	170.5	173.8
39.62	186.0	32.27	184.7	0	192.5	134.4	176.6
0	195.7	10.31	187.3	....	...	132.7	177.2
....	...	0	191.5	....	...	118.0	178.0
						91.1	179.4
						53.1	182.5
						0	193.0

Pr_4NI	Λ	Pr_4NI_3	Λ	Pr_4NI_5	Λ	Pr_4NI_7	Λ
1000	137.4	1000	133.5	1000	130.4	1000	128.0
500.0	146.2	960.8	133.7	500.0	140.1	500.0	138.4
200.0	155.2	500.0	142.7	200.0	149.8	200.0	149.5
163.5	156.4	480.4	143.0	100.0	155.6	100.0	155.4
122.8	158.6	230.6	150.0	50.00	159.3	50.00	159.8
65.29	161.9	200.0	151.2	44.55	159.8	25.00	163.4
60.53	163.1	134.7	154.2	0	169.0	0	170.8
54.81	164.0	100.0	156.1				
36.16	165.0	69.65	158.1				
0	172.5	50.00	159.3				
		0	168.4				

It is seen from Fig. 1 that, as expected, the conductance of the tetrapropylammonium salts is less than that of the tetramethylammonium analogs. In this last series, at higher concentrations, the conductance varies in the direction $I_3^- > I_5^- > I_7^- > I^-$; in the tetrapropyl series, it is $I^- > I_3^- > I_5^- > I_7^-$. In both series the limiting equivalent conductance is highest for the simple iodide, while the limiting conductances for the tri-, penta-

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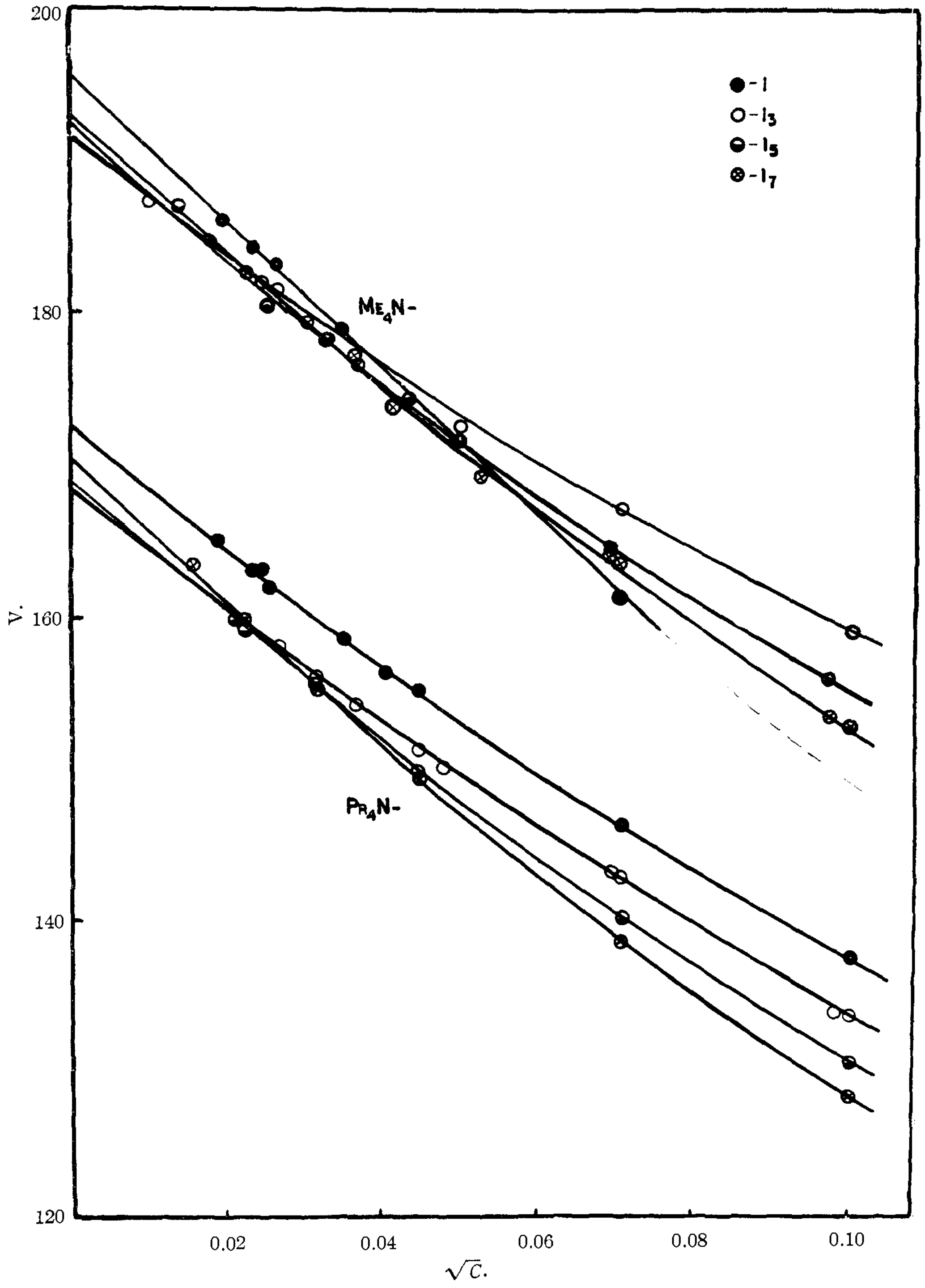

Fig. 1.—The Λ *vs.* $\sqrt{C}$ plots in acetonitrile at 25° for the tetramethyl- and the tetrapropylammonium iodides and polyiodides.

and heptaiodides fall close together. The measurements were repeated for solutions prepared by the addition of iodine to the tetrapropylammonium iodide to produce concentrations equivalent to those of the I_3^-, I_5^- and I_7^- solutions. In the case of the tetramethyl series, the iodine was added to the triiodide because of the very limited solubility of the monoiodide. In all cases a very good agreement was obtained with the solutions prepared by dissolving the corresponding higher polyiodides.

It was observed that solutions of the heptaiodides and enneaiodides did show some increase in conductance with time. The increase was concentration dependent and was much more pronounced in the case of enneaiodide than the heptaiodide. The maximum change for an approximately 4 × 10^{-4} *M* Pr_4NI_9 solution was 5.4%

after 16 hours. It was of the order of 1–2% in 24 hours for the I_7^- solutions and no change was observed with the lower polyiodides.

The conductance of iodine in acetonitrile was measured and was found to increase rapidly with time, confirming previous observations on this system.[14] The rate of increase was concentration dependent, and was greatest in dilute solutions. In order to get at least the order of magnitude of the limiting conductance, all of the measurements were subsequently made exactly 75 minutes after the initial preparation of solutions. By extrapolating the Λ *vs.* $\sqrt{C}$ plot to infinite dilution it was estimated that the Λ_0 value lies between 1.0 and 2.0. Of course, it should be emphasized that although the above value was useful in this work as it indicates, at least approximately, the necessary correction for the conductance of higher iodides, it cannot be claimed that it represents the true limiting conductance for iodine in acetonitrile. This can only be obtained when the reasons for the change in conductance with time will be found. Such a study is now being carried out in this Laboratory.

In order to see whether the decrease in conductance of the higher polyiodides could be due simply to the increased viscosity of the solutions, the viscosity of a 10^{-2} *M* solution of tetrapropylammonium pentaiodide was compared to that of the pure solvent. Since the difference was found to be 1.0 ± 0.2%, increase in viscosity alone cannot account for the decreased conductances of higher polyiodides at that concentration.

As seen from Fig. 1 conductance curves for I_7^-, I_5^- and I_3^- cross each other. It is interesting to note that these crossings occur at very nearly the same concentration for the tetramethyl and the tetrapropyl series. The heptaiodide curve crosses that of the pentaiodide at $C = 9.0 \times 10^{-4}$ in the first case and $C = 8.4 \times 10^{-4}$ in the second. The pentaiodide and the triiodide curves meet at $C = 2.0 \times 10^{-4}$ *M* and 2.70×10^{-4} *M*, respectively. Slightly higher conductance of I_5^- and I_7^- compared to that of I_3^- is, very likely, due to the conductance of free iodine produced by the dissociation. The difference in the limiting equivalent conductances of these ions (obtained by extrapolation of the Λ *vs.* $\sqrt{C}$ plots) is of the same order of magnitude of the limiting equivalent conductance of iodine. If the assumption is made, which seems to be reasonable, that the first crossing indicates complete dissociation of I_7^- ion into I_5^- and I_2, and the second, that of I_5^- ion into I_3^- and I_2, then concentration limits for the existence of I_7^- and I_5^- can be established. Taking the average value for the two series, these limits are, 8.7×10^{-4} *M* for I_7^- and 2.35×10^{-4} *M* for I_5^-.

Although these data do not permit the calculation of the equilibrium constants for the reactions

$$I_7^- \rightleftharpoons I_5^- + I_2 \qquad (1)$$

and

$$I_5^- \rightleftharpoons I_3^- + I_2 \qquad (2)$$

if one makes an arbitrary assumption that at the limiting concentrations the respective polyiodides are dissociated only to the extent of 90%, the *lower limit* of the dissociation constants can be calculated. The values obtained were 7×10^{-3} for eq. 1 and 2×10^{-3} for eq. 2.

In order to ascertain whether any variation in the conductance could be due to ion-pair formation, the limiting equivalent conductance and the ion-pair dissociation constant were calculated by the Fuoss and Shedlovsky method.[15] The results are given in Table II.

TABLE II

LIMITING EQUIVALENT CONDUCTANCE AND ION-PAIR DISSOCIATION CONSTANTS

Salt	Λ_0	*K*
$(CH_3)_4NI$[9]	195.3	3.62×10^{-2}
$(CH_3)_4NI_3$	190.9	5.40×10^{-1}
$(n\text{-}C_3H_7)_4NI$	171.6	1.10×10^{-1}
$(n\text{-}C_3H_7)_4NI_3$	167.5	1.08×10^{-1}

The limiting equivalent conductances and the ion-pair dissociation constants could not be calculated for the higher polyiodides with any degree of accuracy because of their dissociation in dilute solutions. However, since it is known that increase in ionic size tends to increase the ion-pair dissociation constant, and because of the high values already found for the simple iodide and the triiodide, it seems highly doubtful that the higher polyiodides would form ion-pairs to any appreciable extent.

A conductometric titration has been run on an 8×10^{-3} *M* solution of the tetrapropylammonium iodide (Fig. 2). The conductance steadily de-

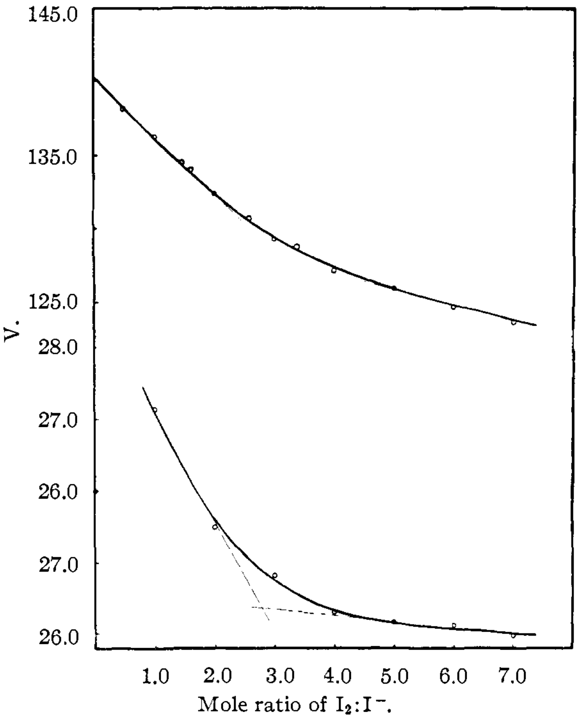

Fig. 2.—Conductometric titration of 8×10^{-3}*M* Pr_4NI with I_2 at 25°: top, acetonitrile solutions; bottom, nitrobenzene solutions.

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[14] A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3722 (1955).

[15] R. M. Fuoss and T. Shedlovsky, *ibid.*, **71**, 1496 (1949).

creases upon addition of iodine. The break in the curve is not sharp but there is a definite change in slope occurring in the neighborhood of the 3/1 ratio of iodine to the iodide ion, which indicates the possibility of the formation of I_7^- ion. The lack of sharpness is undoubtedly due to the instability of the heptaiodide. The continued decrease in conductance, after the 3/1 ratio had been passed, is probably the result of two effects, the increase in the concentration of the heptaiodide ion formed from pentaiodide and excess iodine, and an increase in the viscosity of the solution.

The experiment was repeated in nitrobenzene solutions, where the viscosity effects should be minimized because of the high viscosity of the solvent. Indeed, as seen from Fig. 2, the break appears to be much sharper, and again occurs at the 3/1 ratio of iodine to iodide.

A differential curve, $-\Delta\Lambda/\Delta m$ *vs.* m (m = ratio I_2/I^- for the tetrapropylammonium iodide in acetonitrile), is given in Fig. 3. It is interesting to note that the rate of decrease in conductance is essentially constant until 2/1 ratio of iodine to iodide is reached, that is, until the composition corresponds to that of the I_5^- ion. After this point there is a marked decrease in the rate of variation of conductance which continues gradually until iodine to iodide ratio is 5-6/1. It seems that this change can be explained logically by the gradual formation of the I_7^- ion, from iodine and the pentaiodide. This ion should be fairly unstable at the concentrations used in this titration, and at stoichiometric composition the equilibrium favors the dissociation. As excess iodine is added, more heptaiodide ion is formed and equivalent conductance further decreases. After most of the possible heptaiodide has been formed, the further regular decrease in conductance with additional iodine probably is due to the increased viscosity of solution. These results do not exclude possible formation of a very unstable I_9^- ion at higher concentrations, but they do indicate relative stability of the I_5^- and I_7^- ions at the concentration used in this titration.

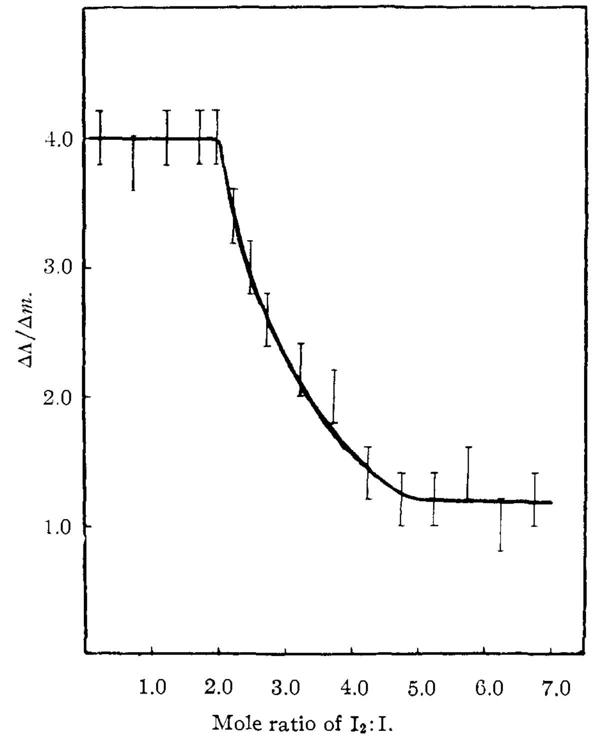

Fig. 3.—Plot of $\Delta\Lambda/\Delta m$ *vs.* m for the titration of 8×10^{-3} *M* Pr_4NI with I_2 in acetonitrile solutions.

A spectrophotometric study was made of solutions of the polyiodides at approximately 3×10^{-5} *M* concentration. The absorption curves for the penta and heptaiodides were identical in shape to that of the triiodide ion, except that the absorption maxima were slightly higher. As before,[8] this difference can be accounted for by the additional absorption of the excess iodine.

In general, it seems that the results of this investigation agree with the ones obtained by earlier workers in this field, in that there is some formation of the higher polyiodide ions, such as pentaiodide and heptaiodide in solutions which are above 10^{-3} molar. The stability of the polyiodide ions decreases rapidly with increasing ionic size and experimental data reported here indicate that I_7^- is the highest polyiodide ion in solutions which are $\geq 10^{-2}$ *M*.

These results seem to be at odds with the reported crystalline structure of these polyiodide ions. It was pointed out already that while there is some indication of the existence of I_5^- ion as an entity, in the solid state, the X-ray work on the heptaiodide seems to show that the limiting polyiodide is I_3^-. The disagreement may be only an apparent one, since it is quite possible that in view of the high polarizability of the iodine molecule we may have ion-induced dipole types of interaction in solutions which would lead to the formation of the penta and heptaiodide aggregates, of rather limited stability.

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