(b).—All other analytical procedures have been described elsewhere.[2]

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

Studies on the Chemistry of Halogens and of Polyhalides. VIII. On the Reaction of Iodine Halides with Aluminum Halides[1]

BY ALEXANDER I. POPOV AND FRANCIS B. STUTE

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Spectrophotometric and electrolytic study of the several systems $AlCl_3$–ICl, $AlBr_3$–IBr, $AlCl_3$–IBr and $AlBr_3$–ICl has been made in acetonitrile solutions. The results obtained indicate that aluminum halide, solvated by acetonitrile, undergoes ionization according to the equation $AlX_3\cdot nCH_3CN \rightleftarrows AlX_m\cdot nCH_3CN^{+3-m} + (3 - m)X^-$ with $m = 2$, 1 or 0. The addition of iodine monochloride or iodine bromide leads to the formation of the corresponding polyhalogen anion $IClX^-$ or $IBrX^-$. A hitherto unreported solid compound $AlBr_3\cdot 2CH_3CN$ has been prepared during this investigation.

Introduction

The reaction of iodine monochloride with aluminum chloride was studied mainly by Fialkov and his co-workers.[2] Physico-chemical measurements such as viscosity, melting point diagrams, electrical conductance and electrical transference were carried out on the iodine monochloride–aluminum chloride system directly, or on concentrated solutions of these compounds in nitrobenzene. The authors report that they have obtained evidence for the formation of the 1:1 addition compound $AlCl_3\cdot ICl$. Where highly concentrated solutions of the $AlCl_3$ + ICl mixtures were electrolyzed, aluminum was shown to be migrating to the anode, and iodine, partially, to the cathode. It was postulated that the initial 1:1 addition compound dissociates to I^+ and $AlCl_4^-$. With increasing amount of iodine monochloride in the solution, the former adds to the chloride coördinated to the aluminum, giving a series of addition compounds culminating in I^+ $[Al(ICl_2)_4]^-$. Throughout this series the cation is the positive iodine while aluminum forms part of the anion.

Indications that this reaction mechanism is not the only possible one were obtained by Gutmann in his study of iodine monochloride as an ionizing solvent.[3] This author reports that most covalent halides, such as $SnCl_4$, $SbCl_5$, VCl_4, etc., when dissolved in liquid iodine monochloride, form solvo-acid type of complexes with an iodine cation, such as $(I^+)_2(SnCl_6)^=$, $I^+(SbCl_6)^-$, $(I^+)_2(VCl_6)^=$, etc., and can be titrated conductometrically with a solvo-base such as potassium chloride. It is interesting to note that such conductometric titrations failed to reveal the presence of $I^+(AlCl_4)^-$.

Since iodine monochloride has a very characteristic absorption spectrum in the visible and the ultraviolet spectral regions, a spectrophotometric study of the iodine monochloride–aluminum chloride system in an appropriate solvent should give some indication as to the nature of addition compounds formed. Also, this technique permits the study of dilute solutions where the reaction mechanism might be quite different from the one found by Fialkov. In this study the measurements were made in acetonitrile solutions since the latter is a polar solvent, has good transparency in the ultraviolet region, and is fairly stable to halogenation. The investigation also has been extended to include aluminum bromide–iodine bromide, aluminum chloride–iodine bromide and aluminum bromide–iodine monochloride systems.

Experimental Part

Reagents.—The preparation of iodine monochloride, iodine bromide and the purification of acetonitrile have been described in a previous publication.[4]

Aluminum chloride was Baker and Adamson resublimed product. It dissolved in acetonitrile with large evolution of heat and upon careful concentration of the resulting solution a solid compound of the formula $AlCl_3\cdot 2CH_3CN$ crystallized out. This compound was previously reported by Perrier.[5] The best method of preparation consists of the addition of aluminum chloride to 200–300 ml. of acetonitrile until saturation, decanting the clear liquid from the excess salt and then concentrating the former by evaporation of the solvent at room temperature in a vacuum desiccator until a crop of white crystals is obtained. The crystals are ground in a dry box, vacuum-dried, and stored in a desiccator. *Anal.* of the product. Calcd. for $AlCl_3\cdot 2CH_3CN$: Al, 12.52; Cl, 49.37; C, 22.40; H, 2.81; N, 13.00. Found: Al, 12.60, 12.62; Cl, 49.26, 49.43, 49.30; C, 22.11; H, 3.23; N, 12.17. Analysis for chloride was carried out by the Volhard method using the improved procedure of Caldwell and Moyer.[6] The aluminum was determined by precipitation with 8-hydroxyquinoline. Carbon, hydrogen and nitrogen were determined by the familiar semi-micro-combustion methods. While Perrier reports a melting point of 50–55°, followed by decomposition at 60°, the product obtained in this investigation had no melting point and did not show any decomposition until 90°.

Aluminum trichloride diacetonitrile is stable and does not lose acetonitrile at ordinary temperatures and pressures. It is hygroscopic, but appears much less reactive to atmospheric moisture than the aluminum chloride itself. It was kept in a desiccator and was used in all subsequent work as a weighing form of aluminum chloride. An analysis for aluminum and chloride carried out on an eight month old sample gave identical results as for the freshly prepared compound.

Aluminum bromide was a laboratory preparation[7] and was obtained as a pure white crystalline solid, with analytical

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[1] Abstracted in part from the Ph.D. Thesis of Francis B. Stute, State University of Iowa, February, 1957.

[2] (a) Ya. A. Fialkov and K. Ya. Kaganskaya, *Zhur. Obshchei Khim*, **16**, 1961 (1946); (b) **18**, 289 (1948); (c) Ya. A. Fialkov and O. I. Shor, *ibid.*, **19**, 1787 (1949); (d) *ibid.*, **23**, 357, 363 (1953).

[3] V. Gutmann, *Z. anorg. Chem.*, **264**, 151 (1951).

[4] A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3277 (1955).

[5] M. G. Perrier, *Compt. rend.*, **120**, 1423 (1895).

[6] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[7] "Inorganic Syntheses," McGraw-Hill Book Co., Vol. III, New York, N. Y., p. 33.

results: Al, 10.11, 10.05%; calcd., 10.11%; Br, 90.23, 90.18%; calcd., 89.89%.

It was found that aluminum bromide reacted with acetonitrile in much the same way as the chloride. Using the method described above, a white solid complex of the formula $AlBr_3 \cdot 2CH_3CN$ was prepared. *Anal.* Calcd.: Al, 7.75; Br, 68.73; C, 13.77; H, 1.73; N, 8.03. Found: Al, 7.81, 7.82; Br, 69.44, 69.91; C, 13.19; H, 1.75; N, 8.08. The compound began to decompose, in a sealed tube, at around 85°. Although the possible existence of this compound has been postulated,[8] it seems that its preparation and properties have not been previously reported in the literature.

Spectrophotometric Measurements.—The absorption spectra of the solutions used in this investigation were obtained with a Cary recording spectrophotometer, Model 11. Silica cells of 1.00 ± 0.01 cm. path length were used. Measurements were made at room temperature of approximately 25°.

Electrolysis.—Electrolysis of the aluminum halide–iodine halide solutions in acetonitrile was carried out in a conventional Hittorf three-compartment apparatus, the cathodic, anodic and the middle compartment each had an approximate capacity of 20 ml. In most cases the solutions were 0.05 *M* in aluminum halide and 0.15 *M* in iodine halide; less concentrated solutions were also electrolyzed, but they were not as convenient from an analytical viewpoint. All solutions were prepared in a dry-box in dry nitrogen atmosphere. A current of approximately five milliamperes was measured with a Weston milliammeter and a silver coulometer was included with the circuit. Bright platinum electrodes, approximately 1 cm.² in area, were used. The duration of electrolysis was usually three hours. All analyses were made on molality basis. After electrolysis the solutions were transferred to stoppered erlenmeyer flasks, diluted with water, and about 0.5–0.8 g. of solid hydrazine sulfate was added to reduce the halogens. Aluminum was determined with 8-hydroxyquinoline. In the $AlCl_3$–ICl system simultaneous determination of halogens was carried out by a method previously described.[9]

Results and Discussion

I. Spectrophotometric Measurements, $AlCl_3$–ICl System.—A series of absorption spectra were obtained of solutions containing iodine monochloride and aluminum chloride in various proportions (Fig. 1). It is seen that as the relative amount of aluminum chloride is increased the absorption maximum shifts from the 358 peak (ICl) to the 338 peak (ICl_2^-).[10]

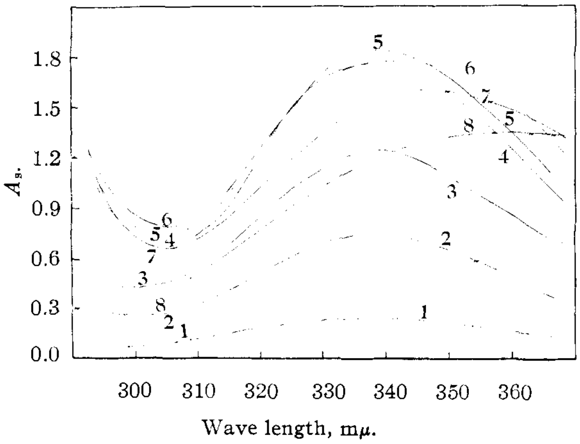

Fig. 1.—Absorption spectra of iodine monochloride and aluminum chloride solutions in acetonitrile. Total concentration, 1.0 × 10^{-2} *M*. Mole fraction of ICl: (1) 0.1; (2) 0.3, (3) 0.5; (4) 0.7; (5) 0.75; (6) 0.9; (7) 0.95; (8) 1.0.

These results indicate that the iodine monochloride reacts with the chloride ions provided by the aluminum chloride. A method of continuous variation[11] was then used to determine the ratios in which the two halides react and the results are given in Fig. 2. It is seen that the maximum concentration of the ICl_2^- ion occurs at 3:1 ratio of ICl to $AlCl_3$ and the over-all reaction can be written as

$$AlCl_3 + 3ICl \rightleftharpoons Al(ICl_2)_3$$

However, this is not the only occurring reaction since at 305 and at 360 mμ the maximum is shifted toward higher ICl/$AlCl_3$ ratios. Therefore, it can be concluded that with an excess of interhalogen more than three iodine monochloride molecules are capable of reacting with aluminum chloride. Numerous repetitions of this study were made varying the total concentration of the solutions; in every case the position of the respective maxima remained unchanged although the peak heights varied by an amount greater than would be expected from the experimental error. There was a marked increase in the absorption values with time; however, the position of the maxima did not change. At 358 mμ (the ICl maximum), the molar absorbancy indices for ICl and for ICl_2^- are, respectively, 135 and 180. Assuming that the conversion of ICl to ICl_2^- is complete at 3:1 ratio of ICl to $AlCl_3$, the absorption for the 1 × 10^{-2} *M* solution containing 0.9 mole fraction of ICl should be 1.350. The actually observed value is 1.525.

The excess absorption can only be explained by the reaction of the excess of iodine monochloride with the solvated Al^{+++} ion. Attempts were made to obtain the absorption spectra of ICl with non-halogen salts of aluminum, such as the perchlorate or the nitrate. However, attempts to prepare these salts in anhydrous form were unsuccessful and the hydrated salts gave inconclusive results. It has been established that iodine monochloride solutions in acetonitrile are unstable in the presence of moisture[4] and tend to form ICl_2^- ion and presumably I^+.

$AlBr_3$–IBr System.—The above experiments were repeated with solutions containing aluminum bromide and iodine bromide. The measurements were made in the 350–450 mμ region. Iodine bromide has an absorption maximum at 416 mμ with a_m = 322; the iododibromide ion, IBr_2^-, has an absorption maximum at 370 mμ with a_m = 606. Aluminum bromide does not absorb in this region. The results of the continuous variation study on solutions with a total concentration of 5 × 10^{-3} *M* are shown in Fig. 2. All the maxima fall close to the 3:1 ratio of IBr/$AlBr_3$. The absorption curve for iodine bromide upon addition of aluminum bromide shifts to the IBr_2^- spectrum. When the mole fraction of iodine monobromide was 0.75, the observed absorbance at 370 mμ was 2.25. On the basis of a complete reaction $AlBr_3 + 3IBr \rightarrow$ Al-

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[8] E. Wertyporoch and B. Adamus, *Z. physik. Chem.*, **168**, 31 (1934).

[9] A. I. Popov, D. F. Geske and N. C. Baenziger, THIS JOURNAL, **78**, 1793 (1956).

[10] A. I. Popov and E. H. Schmorr, *ibid.*, **74**, 4672 (1952).

[11] P. Job, *Ann. Chim.* [10] **9**, 113 (1928).

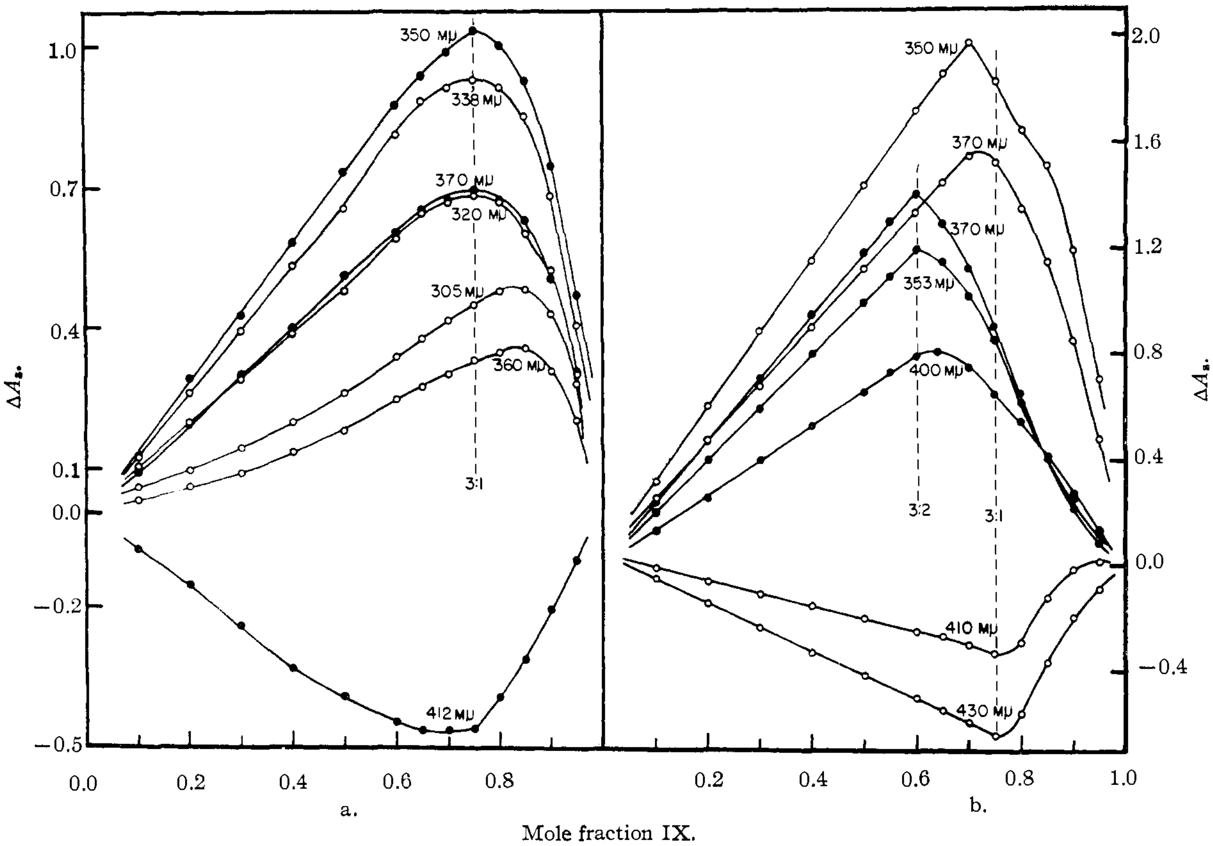

Fig. 2.—Continuous variation study: (a) ○, $AlCl_3$–ICl; ●, $AlCl_3$–IBr; (b) ○, $AlBr_3$–IBr; ●, $AlBr_3$–ICl.

$(IBr_2)_3$ the calculated absorbance due to the formed IBr_2^- ion is 2.27.

$AlCl_3$–IBr and $AlBr_3$–ICl Systems.—By analogy with previous results, it would be expected that in these two cases the addition of the interhalogen to the aluminum halide would lead to the formation of the mixed polyhalide ion $IBrCl^-$. However, it has been shown that $IBrCl^-$ ion undergoes a disproportionation into IBr_2^- and ICl_2^- ions.[12] The addition of an excess of the bromide ion shifts the $IBrCl^-$ absorption to that of IBr_2^- while addition of chloride ion shifts it to that of ICl_2^-. This, of course, complicates the method of continuous variation since it would be expected that in the $AlCl_3$–IBr system, at high $AlCl_3$/IBr ratios, some of the absorption will be due to ICl_2^-; likewise, the $AlBr_3$–ICl solution with an excess of $AlBr_3$ would yield IBr_2^-.

As seen from Fig. 2, these predictions were realized. In the case of $AlCl_3$–IBr system, the first absorbing species formed upon addition of iodine bromide to aluminum chloride is probably ICl_2^-, which has only a slight absorption in the 350–400 mμ region. In this case the interference is slight and a maximum falls at 3:1 ratio. On the other hand, when bromide ion is in excess ($AlBr_3$–ICl system), there is formation of IBr_2^- ion, which has a strong absorption in the 350–400 mμ region (a_m = 606 at 370 mμ).[12] In this case the method of continuous variation is unreliable, and the maximum falls short of the 3:1 ratio as expected. However, the solution containing 3:1 ratio of interhalogen to aluminum halide gave, for both systems, identical absorption curves at equal concentration. This proves that in both cases the absorbing species is the $IBrCl^-$ ion.

In order to ascertain which of the polyhalogen ions were actually present in the system $AlBr_3$–ICl, the solutions containing 0.6, 0.7, 0.8 and 0.9 mole fractions of iodine monochloride were diluted 50-fold and their absorption spectra were measured in the ultraviolet region. The solution containing 0.6 mole fraction of iodine monochloride still showed a maximum at 256 mμ which corresponds to the IBr_2^- ion.[12] With increasing amounts of iodine monochloride the characteristic peak of $IBrCl^-$ at 237 mμ was apparent and when the mole fraction of the interhalogen rose to 0.9 the corresponding ultraviolet peak was at 229 mμ which closely corresponds to the ICl_2^- absorption maximum at 227 mμ.

II. Electrolysis Experiments.—The electrolysis of aluminum halides–iodine halides solutions were carried out as described in the Experimental Part. The results are summarized in Table I.

The data represented in Table I seem to indicate clearly that in all cases the aluminum, at least preferentially, migrates to the cathode, and that the anion complex $AlX_4 \cdot nIX^-$ found in nitrobenzene solution, cannot be a major component of the systems studied here. Halogen analyses were carried out after the electrolysis of $AlCl_3$–ICl solutions and it shows (Table I) that iodine and chlorine migrate to the anode in the ratio essentially

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[12] A. I. Popov and R. F. Swenson, This Journal, **77**, 3724 (1955).

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

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

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.

IOWA CITY, IOWA

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(13) Z. A. Sheka, *Raboty Khim. Rastvorov i Kompleks. Soed. Akad. Nauk., S.S.R.*, 113 (1954).

(14) F. Fairbrother and N. Scott, *J. Chem. Soc.*, 452 (1955).

(15) D. D. Eley and P. J. King, *ibid.*, 2517 (1952).

(16) M. I. Ushakov, *J. Russ. Phys. Chem. Soc.*, **61**, 2089 (1929).

(17) A. I. Popov and N. E. Skelly, unpublished work.

[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]

BY ALEXANDER I. POPOV, RALPH H. RYGG AND NORMAN E. SKELLY

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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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