ments, especially for the case of iodine–pyridine solutions.[13]

The reasons for the slow reactions have been attributed either to a gradual halogenation of the solvent[13b,c] or to a reaction with traces of moisture and/or other impurities.[13e] In a recent work of Buckles and Mills[4] the authors report that they have found no evidence for a reaction of iodine monochloride with the solvent. It seems from the data obtained in this investigation that the evidence favors a slow reaction with the moisture because of the drastic change in the rate of increase of electrical conductance when the measurements were made in an enclosed system. It is evident, however, that a considerable amount of further work is needed to elucidate completely the behavior of interhalogen compounds in various solvents.

Acknowledgment.—The authors gratefully acknowledge the support of a part of this project by the Research Corporation. They also wish to express their appreciation to Dr. Robert E. Buckles of this Laboratory for many helpful discussions on this problem.

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Studies on the Chemistry of Halogens and of Polyhalides. V. Spectrophotometric Study of Polyhalogen Complexes in Acetonitrile and in Ethylene Dichloride

BY ALEXANDER I. POPOV AND ROBERT F. SWENSEN

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Absorption spectra of several polyhalogen complexes have been recently determined in various solvents,[1] but only in the case of the iododichloride and iodotetrachloride ions in acetonitrile, has the investigation been carried out with thoroughness, and the absorption characteristics have been determined. This work was undertaken in order to obtain precise data on the absorption spectra of the more common of the remaining polyhalide anions such as the IBr_2^-, I_2Br^-, $IBrCl^-$, I_2Cl^-, I_3^- and Br_3^-. It was of interest to determine the absorption spectra in polar and non-polar solvents. For the first type, acetonitrile seems to be a good choice because of high dielectric constant (36.5 at 25°), fair resistance to halogenation, and especially its transparency down to 200 mμ. The choice of the second solvent was primarily determined by the limited solubilities of ionic polyhalides in non-polar liquids. The best possibility seems to be ethylene dichloride ($D = 10.2$ at 25°) which can dissolve sufficient amounts of the tetraalkylammonium polyhalides for spectrophotometric measurements and is transparent down to 235 mμ.

Experimental Part

Apparatus.—All spectrophotometric measurements were made on a Cary recording spectrophotometer, model 11, under conditions described in previous publications.[1b]

Solvents.—Acetonitrile was obtained from the Matheson, Coleman and Bell Co., and purified by methods already described.[1b] Ethylene dichloride was obtained from the Union Carbide and Carbon Co. It was purified by shaking it with several portions of sulfuric acid until the acid layer remained clear, washing it with copious amounts of water, followed by washing with a dilute solution of sodium bicarbonate and again with water. Since ethylene dichloride forms an azeotropic mixture with water, the latter was removed by distillation and the last traces of moisture were further removed by refluxing the solvent for several hours over phosphorus pentoxide and then distilling it twice from the same reagent. The boiling point of the solvent was 83.5° at 760 mm.

It was found important to check the purity of ethylene dichloride by the following procedure. A small amount of bromine was added to a couple of hundred milliliters of the solvent and the amount of halogen was titrated iodometrically in an aliquot portion. The titration was repeated the next day and if no change in bromine concentration was observed, the solvent was used for subsequent spectrophotometric work.

Polyhalogen Complexes.—The following polyhalogen complexes were prepared according to the general directions of Chattaway and Hoyle[2]: Tetramethylammonium diiodobromide, tetramethylammonium iododibromide, tetramethylammonium iododichloride, tetramethylammonium iodobromochloride and tetramethylammonium triiodide. The tetrabutylammonium tribromide and the tetrapropylammonium iododibromide were, respectively, furnished by L. Harris and N. E. Skelly of this Laboratory. The purity of preparations was checked by iodometric titrations and by comparison of the melting points with those in the literature,[2] and satisfactory agreements were obtained in each case.

Considerable difficulties were experienced in the preparation of the tetramethylammonium diiodochloride which, to the authors' knowledge, has not been, as yet, described in the literature. The addition of one mole of iodine to tetramethylammonium chloride in methanol solution resulted in the formation of a mixture of the diiodochloride, tetraiodochloride and of pentaiodide ions. Somewhat better results were obtained in using isopropyl alcohol as a solvent. Upon cooling the solution containing a mixture of iodine and tetramethylammonium chloride, first a mixture of the tetraiodochloride and of diiodochloride was obtained, but upon filtering and letting the solution stand overnight, a crop of bronze-red crystals was obtained which analyzed to be the diiodochloride. The crystals had a m.p. of 102°. The compound is rather unstable and slowly gives up iodine. Complete decomposition was observed after several weeks. The absorption spectra of the diiodochloride solutions were determined on freshly prepared samples.

Solutions.—Preliminary experiments have indicated that the solutions of polyhalogen complexes in purified acetonitrile and ethylene dichloride are quite stable for at least 24 hours. The solutions were prepared by dissolving a weighed amount of a salt in a given volume of the solvent and then diluting to required concentrations. All measurements were made on solutions prepared on the same day.

Suppression of Dissociation.—Since it is known that the polyhalide ions dissociate in acetonitrile, and since it was desired to obtain the true molar absorbancy indices for these species, the absorption spectra were determined on solutions containing an excess of the dissociated halide ion in the form of the corresponding tetramethylammonium salt. The halide salt was added until no further change in the absorption spectra was observed. None of the simple halides absorbed appreciably at the wave lengths investigated.

Results and Discussion

The absorption spectra of the polyhalogen complexes in the two solvents are given in Figs. 1 and 2 and the absorption data and the peak maxima are shown in Table I. All of the polyhalogen complexes

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(1) (a) A. I. Popov and E. H. Schmorr, THIS JOURNAL, **74**, 4672 (1952); (b) A. I. Popov and J. N. Jessup, *ibid.*, **74**, 6127 (1952); (c) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 3116, 4845, 6021 (1954).

(2) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

exhibit a low peak in the visible or near ultraviolet and a very high absorption peak in the far ultraviolet. Since the difference in the molar absorbancy indices of the two peaks is at least of two magnitudes, separate solutions have to be prepared for measuring the absorption at the two wave length regions. It is interesting to note that in the case of the iododibromide and iodobromochloride if a too dilute solution is used for measurements at longer wave lengths, the low absorption peaks can be missed.

TABLE I

ABSORPTION CHARACTERISTICS OF POLYHALOGEN COMPLEXES IN ACETONITRILE AND IN ETHYLENE DICHLORIDE

	Acetonitrile				Ethylene dichloride			
Anion	Max_1 (mμ)	a_{m1}	Max_2 (mμ)	a_{m2}	Max_1 (mμ)	a_{m1}	Max_2 (mμ)	a_{m2}
ICl_2^-	336	310	227	54500	338	414	..	...
Br_3^-	269	55000	..	...	273	54000	..	...
I_3^-	360	25500	291	38800	362	25000	292	45800
I_2Br^{-a}	351	11600	280	40600	..	...	..	...
$IBrCl^-$	356	413	237	38700	357	427	242	35000
IBr_2^-	370	606	256	54000	370	639	360	55000
$I_2Cl^{-a,b}$	360	9800	288	23000	..	...	..	...
$I_2Cl^{-a,b}$	261	19000	227	10000	..	...	..	...

[a] Compounds were insoluble in ethylene dichloride. [b] Approximate values. Because of disproportionation no effort was made to suppress the dissociation.

In general, the polyhalide anions dissociate to some extent giving a halogen or an interhalogen molecule and a halide ion. The latter is usually the more electronegative of the halogens present. Thus, in the case of ICl_2^- we have a dissociation into ICl and Cl^-, the I_2Br^- ions dissociate into $I_2 + Br^-$, etc. Addition of the tetraalkylammonium chloride in the first case, and of the tetraalkylammonium bromide in the second, produces simply an increase in the absorption peak without change in the position of the respective maxima.

If this was the general rule, one would expect the iodobromochloride ion to dissociate into Cl^- and IBr; however, the addition of an excess of the chloride ion produces a shift in the absorption maximum to 227 mμ, which is the characteristic peak of the ICl_2^- ion. The addition of excess bromide ion shifts the peak to 256 mμ which coincides with that of the IBr_2^- ion. It seems, therefore that the $IBrCl^-$ ion can disproportionate to some extent in solution and upon addition of the

$$2IBrCl^- \rightleftarrows IBr_2^- + ICl_2^- \qquad (1)$$

chloride or bromide ion in excess, we have, respectively

$$IBr_2^- + 2Cl^- \longrightarrow ICl_2^- + 2Br^- \qquad (2)$$

$$ICl_2^- + 2Br^- \longrightarrow IBr_2^- + 2Cl^- \qquad (3)$$

It is, of course, well known that the addition of the iodide ion to a solution of a polyhalogen complex containing chlorine or bromine invariably results in the formation of the triiodide ion. This reaction, in fact, is the basis of iodometric titrations of the polyhalides.

The disproportionation of the diiodochloride ion is much more pronounced than that of the iodobromochloride. Its absorption spectrum in acetonitrile (Fig. 1, curve 5) shows four peaks, two of which (360 and 288 mμ) coincide with those of the triiodide ion, and the one at 227 mμ is that of the iododi-

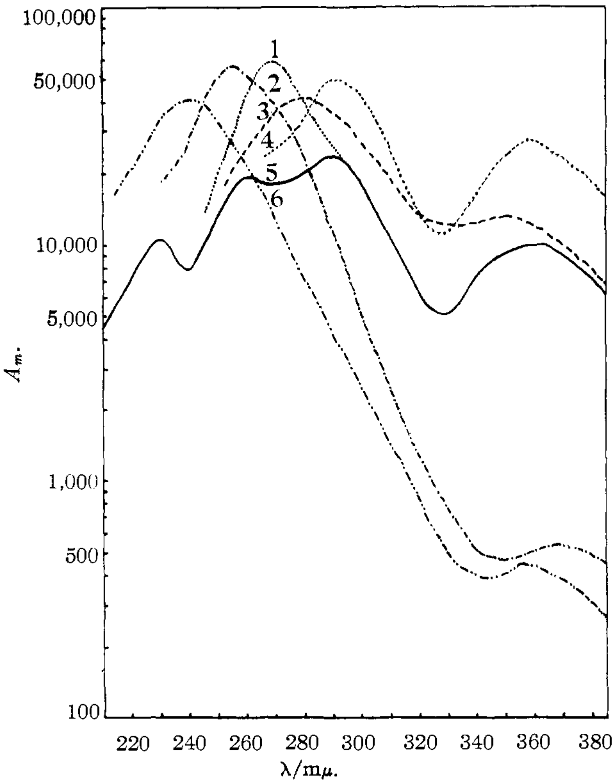

Fig. 1.—Absorption spectra of polyhalogen complexes in acetonitrile solutions: 1, Bu_4NBr_3; 2, Me_4NIBr_2; 3, Me_4NI_2Br; 4, Me_4NI_3; 5, Me_4NI_2Cl; 6, $Me_4NIBrCl$.

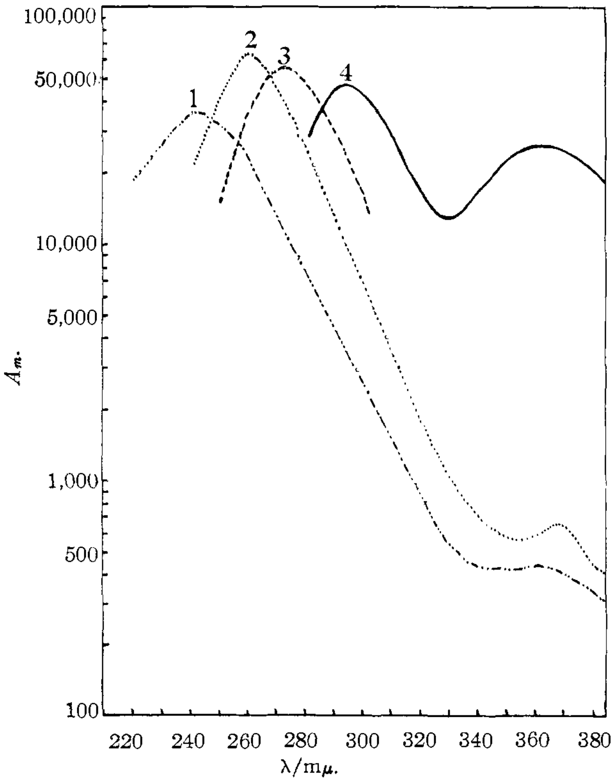

Fig. 2.—Absorption spectra of polyhalogen complexes in ethylene dichloride solutions: 1, $Me_4NIBrCl$; 2, Me_4NIBr_2; 3, Bu_4NBr_3; 4, Me_4NI_3.

chloride ion.[3] The high peak at 261 mμ does not coincide with any of the other known maxima of the polyhalide ion and is, therefore, probably due to the I_2Cl^- ion.

Another interesting bit of information given by Table I is that there is not much difference in the absorption spectra of the polyhalides in acetonitrile and in ethylene dichloride. However, from the study of electrical conductances of these complexes in the two solvents,[4] it is known that while the polyhalides are strong electrolytes in acetonitrile, they are considerably associated in ethylene dichloride, the dissociation constants being of the order of 1×10^{-4}. Therefore in ethylene dichloride they are present primarily as ion pairs. It can be concluded that the absorption spectra of the polyhalide ions are not appreciably affected by the ion-pair formation.

(3) It is evident that in view of high absorption at 360 mμ the 338 peak of ICl_2^- will be masked.

(4) (a) A. I. Popov and N. E. Skelly, This Journal, **76**, 5309 (1954); (b) A. I. Popov and N. E. Skelly, *ibid.*, **77**, 3722 (1955).

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The Diffusion Coefficient of Nickel(II) in Sodium Perchlorate Solutions

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In connection with other work the diffusion coefficient of Ni(II) was determined in both dilute and concentrated sodium perchlorate at 25°. The capillary cell technique essentially as employed by Wang[1] was used with Ni^{66} as the radiotracer. The solutions were slightly acid to prevent hydrolysis, and the nickel concentration was approximately 3 millimolar to make specific adsorption on the capillary walls negligible.

Experimental.—Ni^{66} tracer was produced by the bombardment of Bi_2O_3 powder with 340 Mev. protons. Ni carrier was added, and the nickel fraction of the target was taken and purified by standard methods, lastly being weighed as the dimethylglyoximate. The Ni precipitate was then dissolved in hot concentrated HNO_3, the solution was evaporated to dryness and the nickel converted to the perchlorate with concentrated $HClO_4$. The salt formed on evaporating this solution was then recrystallized twice from aqueous solution, and finally was dissolved in a known quantity of the perchlorate solution to be studied. This solution was used as the stock solution for the capillary cells. An identical solution for the large diffusion bath was prepared using non-radioactive nickel perchlorate.

The capillary cells used were about 7 cm. long and 2 mm. in diameter to allow the use of fairly large samples, for the radioisotope was difficult to prepare with high specific activity.

The capillary cells were filled with tracer solution and placed in the diffusion bath previous to total immersion for about 20 minutes to allow them to come to the temperature of the constant temperature bath, which was maintained at 25.00 ± 0.03°. Stirring in the diffusion bath was not deemed necessary for the accuracy that was desired. Diffusion was allowed to take place for about 2.5–3 days, at which time the cells were removed from the diffusion bath and the entire contents taken and sampled.

It was found that with large quantities of $NaClO_4$ on the counting plate, reproducible counts could not be obtained, necessitating the following sampling scheme, which was applied to both the stock tracer solution and the contents of the cells after diffusion.

The nickel in the samples was extracted in a centrifuge cone with dimethylglyoxime dissolved in chloroform, the succeeding extracts being removed with a transfer pipet into a weighed 25-ml. glass-stoppered erlenmeyer flask. Each time the $CHCl_3$ was evaporated with a heat lamp, and, after a sufficient number of extractions, the dimethylglyoximate was destroyed with hot concentrated HNO_3. The resulting solution was concentrated under the heat lamp, and a weighed portion was taken and placed on a platinum counting plate and evaporated.

The samples were then counted with a thin mica window Geiger–Müller tube in conjunction with a scaler on each of three succeeding days. The 56-hour Ni^{66} is in equilibrium with the 5-minute Cu^{66} which decays to stable Zn^{66}. The 2.63 Mev. β-rays from the Cu^{66} primarily are those being counted, with a small contribution from the weak betas from the Ni^{66}. A total of at least 100,000 counts was taken in each case to reduce the probable statistical deviation to about 1%, and each count was corrected for coincidences and background. Since Ni^{66} has a 56-hour half-life, and in some cases the size of the samples necessitated a counting period of up to 300 minutes, each count was also corrected for decay during the counting period. All counts were then extrapolated to the same time, chosen as the middle of the counting period in the entire experiment. The ratio of the average concentration after diffusion to the initial concentration was then determined for each cell. From these ratios the diffusion coefficient was found by successive approximations to the equation

$$\frac{C_{av}}{C_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2\pi^2 DT}{4L^2}\right]$$

where C_{av} is the averaged concentration after diffusion, C_0 is the initial concentration, D is the diffusion coefficient in cm.²/sec., T is the total diffusion time in seconds, and L is the length of the cell in centimeters.

Results.—In each experiment four cells were used. The average values obtained for the diffusion coefficients in the solutions studied are given in Table I.

TABLE I

$NaClO_4$, M	$HClO_4$, M	$Ni(ClO_4)_2$, M	$D \times 10^5$, cm.²/sec.
0.1	0.001	0.00323	0.60 ± 0.06
3.0	.001	.00360	.56 ± .06

The values of the diffusion coefficients are seen to be reasonable when compared with the limiting value of 0.69×10^{-5} obtained from conductance data.[2] They suggest that there has been no change in the nickel species in going to the more concentrated solution. It is also of interest to note that the value 0.60×10^{-5} cm.²/sec. fits our unpublished polarographic data in 0.1 M $NaClO_4$ to within 2% when the improved diffusion current equation of Lingane and Loveridge[3] is used.

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(1) J. H. Wang, This Journal, **74**, 1182 (1952).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Edition, Vol. 1, Interscience Publishers, New York, N. Y., 1952, p. 52.

(3) Reference 2, p. 63.