

of mannitol gave a boron content equivalent to 31.0 cc. of B_5H_9 . The calculated H_2/B_5H_9 ratio was 12.1. In another experiment 6.56 cc. of B_5H_9 (by titration) yielded 78.4 cc. of H_2 to give a ratio of 11.9.

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Dissociation of Quaternary Ammonium Polyhalides in Trifluoroacetic Acid¹

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During the investigation of quaternary ammonium dichloriodides² and of the quaternary ammonium tetrachloriodides³ it was found that the visible and ultraviolet absorption spectra of the salts in trifluoroacetic acid were identical with those of the halogens expected from the complete dissociation of the polyhalide ion. In Table I are summarized similar results for other quaternary ammonium halides. In each case the hydrogen halide derived from the most electronegative halogen atom present in the polyhalide ion must have been formed also. Little ionization of the hydrogen halide would be expected in trifluoroacetic acid, which is such a strong proton donor that the trifluoroacetate ion present would show little tendency to act as a proton acceptor, and the acid itself would show even less. Consequently it is not unreasonable that the concentration of the halide ion in each case would be so low that the molecular halogen present in the dilute solution used would not interact to give any detectable amount of polyhalide ion. The dissociation cannot be explained by competitive complexing of the molecular halogen with the solvent since such acidic solvents as trifluoroacetic acid show⁴ little tendency to enter into such complex formation.

TABLE I

MOLAR ABSORBENCY INDICES OF ABSORPTION SPECTRA PEAKS OF HALOGENS AND QUATERNARY AMMONIUM POLYHALIDES IN TRIFLUOROACETIC ACID

Compound	Concn., $M \times 10^3$	λ , $m\mu$	a_m
I_2	1.44	512	815
Me_4NI_3	1.55	513	806
Bu_4NI_3	1.40	513	805
Me_4NI_5	0.64	512	1624
$Me_4NI_4Cl^a$	0.72	512	1682
Br_2	13.9	411	160
Me_4NBr_3	14.2	410	159
Bu_4NBr_3	12.8	410	157
IBr	11.1	487	308
Me_4NIBr_2	7.7	487	314
$Me_4NIBrCl$	7.4	486	294

^a Iodometric analysis showed this compound to be impure. The percentage of reducible halogen was 3% high.

The addition of excess tetramethylammonium chloride, which showed little absorption in the

(1) Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission.

(2) R. E. Buckles and J. F. Mills, *THIS JOURNAL*, **76**, 4845 (1954).

(3) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 3716 (1954).

(4) (a) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953); (b) J. G. Bower and R. L. Scott, *ibid.*, **75**, 3583 (1953); (c) L. I. Katzin and J. J. Katz, *ibid.*, **75**, 6057 (1953).

region studied, had little effect on the spectrum of tetramethylammonium tetraiodochloride. It did lower the iodine bromide peak shown by tetramethylammonium iodobromochloride at 486 $m\mu$ from a molar absorptivity index (molar extinction coefficient) of 294 to 258. Absorption in the region 260–400 $m\mu$ was increased at the same time. Such changes might indicate some suppression of the dissociation and formation of the iodobromochloride ion especially since a peak of molar absorptivity index around 3.5×10^4 near 240 $m\mu$ and one of molar absorptivity index about 400 near 355 $m\mu$ have been observed⁵ for this ion in ethylene chloride and in acetonitrile.

Attempts to suppress the dissociation in a $7.08 \times 10^{-4} M$ solution of tetramethylammonium triiodide with tetramethylammonium iodide ($3.4 \times 10^{-3} M$) led to the disappearance of the violet color and the precipitation of the triiodide salt. When 2.5 ml. of water was present with the trifluoroacetic acid in 50 ml. of solution a red-violet solution was obtained. The absorption spectrum showed an iodine peak of molar absorptivity index 706 at 500 $m\mu$ and very high absorption at wave lengths below 400 $m\mu$ which would be expected of triiodide ion.

In the course of the investigation it became necessary to re-examine the absorption spectra of iodine, bromine and iodine chloride in trifluoroacetic acid. It was observed that the values for the molar absorptivity indices reported^{1a} for these halogens were consistently too low. Evidently a combination of difficulties encountered in making up the stock solutions and standardizing them had not been completely surmounted in the earlier investigation. The higher values obtained in the present investigation and given in Table I actually are more consistent with the conclusions reached in the earlier work than are the values which were reported at that time. That is, the solutions of the halogens in trifluoroacetic acid behave spectrophotometrically like those in non-complexing solvents. This general relationship is shown in Fig. 1 for iodine bromide, which was not included in the original study.

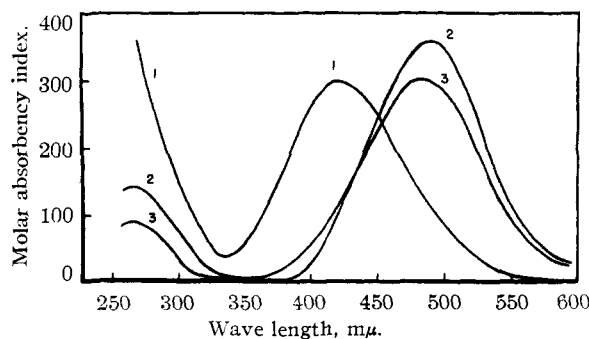


Fig. 1.—Absorption spectra of iodine bromide (1) $5.3 \times 10^{-3} M$ in anhydrous acetic acid, (2) $6.6 \times 10^{-3} M$ in carbon tetrachloride and (3) $1.11 \times 10^{-2} M$ in trifluoroacetic acid.

Experimental Part

Materials.—The solvents and the halogens were purified as described^{4a} for the earlier investigation. The polyio-

(5) A. I. Popov and R. F. Swenson, private communication.

dides⁶ and the tribromides^{6b,7} were available from earlier investigations. Pure iodine bromide as well as samples of tetramethylammonium dibromiodide (m.p. 192°), tetramethylammonium iodobromochloride (m.p. 204–205°) and tetramethylammonium tetraiodochloride (m.p. 108–109°) were kindly supplied by Dr. A. I. Popov and Mr. R. F. Swenson of this Laboratory.

Stock Solutions.—Homogeneous solutions of polyhalides or halogens in trifluoroacetic acid could be prepared only when the solute and solvent were shaken together long and vigorously. Often periods of shaking several hours in length were necessary. Particular care was taken to use tightly stoppered containers when handling the solutions in order to avoid halogen losses caused by volatility. A 5- or 10-ml. sample was mixed with at least 10 times its volume of water and the resulting aqueous solution was immediately subjected to an iodometric analysis for reducible halogen.

Absorption Spectra Measurements.—Measurements were carried out at 25° in calibrated silica cells of path length 1.00 ± 0.01 cm. with a Cary Model 11 recording spectrophotometer. The uniform nomenclature and symbology suggested by the National Bureau of Standards⁸ have been used throughout this note.

(6) (a) R. E. Buckles, J. P. Yuk and A. I. Popov, *THIS JOURNAL*, **74**, 4379 (1952); (b) R. E. Buckles and J. P. Yuk, *ibid.*, **75**, 5048 (1953).

(7) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, *ibid.*, **73**, 4525 (1951).

(8) National Bureau of Standards, Letter-Circular LC-857 (1947).

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A Study of Alkaline Solutions of Zinc Oxide

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In a recent paper¹ it was shown that in concentrated alkaline solutions dissolved zinc is present primarily as $Zn(OH)_4^{--}$. Since, however, claims have been made for the identification of a hydrogen zincate ion in such solutions^{2–4} an attempt was made to verify this in dilute alkaline solutions where such ions are more likely to occur. This attempt involves the determination of the solubility of zinc oxide in alkaline solutions.

Since it was previously shown¹ that in strongly alkaline solutions $Zn(OH)_4^{--}$ was the highest hydroxyl containing species of dissolved zinc it can be assumed that all the dissolved zinc in dilute alkaline solutions will be in the form of ZnO or $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{--}$. Recently a claim has been made for the existence of $Zn(OH)_6^{4-}$ ions in alkaline solutions.⁵ However, if the authors would have used the mean activity instead of the stoichiometric concentration of the hydroxyl ions in the Nernst equation, their results would have shown that $Zn(OH)_4^{--}$ is the highest hydroxyl containing zinc ion present.

If S represents the total solubility of zinc in such solutions, then

$$S = M_{Zn(OH)_2} + M_{Zn(OH)_3^-} + M_{Zn(OH)_4^{--}} \quad (1)$$

(1) T. P. Dirkse, *J. Electrochem. Soc.*, **101**, 328 (1954).

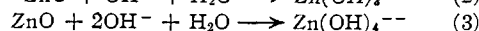
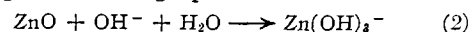
(2) J. H. Hildebrand and W. G. Bowers, *THIS JOURNAL*, **38**, 785 (1914).

(3) G. W. Heise and E. A. Schumaker, *Trans. Electrochem. Soc.*, **62**, 383 (1932).

(4) M. P. Bernheim and M. Quintin, *Compt. rend.*, **230**, 388 (1950).

(5) K. Kordesch and F. Martinola, *Monatsh.*, **84**, 39 (1953).

Assuming the following equilibria



for which

$$K_1 = [M_{Zn(OH)_3^-} \times y_{Zn(OH)_3^-}] / [M_{OH^-} \times y_{OH^-} \times a_{H_2O}] \quad (4)$$

$$K_2 = [M_{Zn(OH)_4^{--}} \times y_{Zn(OH)_4^{--}}] / [(M_{OH^-})^2 \times (y_{OH^-})^2 \times a_{H_2O}] \quad (5)$$

then

$$S = M_{Zn(OH)_2} + [K_1 \times M_{OH^-} \times y_{OH^-} / y_{Zn(OH)_3^-}] + [K_2 \times (M_{OH^-})^2 \times (y_{OH^-})^2 / y_{Zn(OH)_4^{--}}] \quad (6)$$

The activity of water is omitted here since in dilute alkaline solutions this value approaches one. It may further be assumed that in a given solution the activity coefficients of all singly charged ions are the same. Equation 6 then becomes

$$S = M_{Zn(OH)_2} + K_1 \times M_{OH^-} + K_2 \times (M_{OH^-})^2 \times (y_{OH^-})^2 / y_{Zn(OH)_4^{--}} \quad (7)$$

From the Debye-Hückel theory

$$\log y_{\pm(1-1)} = -A\sqrt{\mu} / (1 + Ba_1\sqrt{\mu})$$

$$\text{and } \log y_{\pm(1-2)} = -2A\sqrt{\mu} / (1 + Ba_1\sqrt{\mu})$$

where the numbers in parentheses refer to the type of ionic species present. From this it follows that

$$\log y_{\pm(1-2)} = 2 \log y_{\pm(1-1)} \quad (8)$$

if $a_i(1-1) = a_i(1-2)$ which is a reasonable assumption for the systems studied here. From equation 8 it also follows that

$$y_{\pm(1-2)} = [y_{\pm(1-1)}]^2 \quad (9)$$

The following series of relationships can then be made

$$\frac{(y_{OH^-})^2}{y_{Zn(OH)_4^{--}}} = \frac{(y^+)^2(y_{OH^-})^2}{(y^+)^2(y_{Zn(OH)_4^{--}})} = \frac{[y_{\pm(1-1)}]^4}{[y_{\pm(1-2)}]^3} = \frac{[y_{\pm(1-1)}]^4}{[y_{\pm(1-1)}]^6} = \frac{1}{[y_{\pm(1-1)}]^2} \quad (10)$$

Substituting this relationship in equation 7

$$S = M_{ZnO} + K_1 \times M_{OH^-} + K_2 \times (M_{OH^-})^2 / [y_{\pm(1-1)}]^2 \quad (11)$$

Although the Debye-Hückel equation holds only in dilute solutions still it is likely that a ratio of activity coefficients determined from this equation will hold up to somewhat higher ionic strengths.

Experimental

All solubilities were determined at 25 ± 0.1°. The best grade of powdered zinc oxide, potassium hydroxide and sodium hydroxide was used. The alkaline solutions were prepared by dilution of saturated solutions of potassium hydroxide and sodium hydroxide. Precautions were constantly taken to exclude carbon dioxide. The solutions were stored in polyethylene bottles and after zinc oxide was added the mixtures were kept in the constant temperature bath for a month. During this time they were shaken frequently. Finally they were carefully filtered using fritted glass filtering crucibles. The analysis for zinc was done amperometrically.⁶ The mean activity coefficients of the hydroxyl ion were determined from the data given in the book of Harned and Owen.⁷

Results

Figure 1 gives a summary of the data obtained. It will be noted that the results for sodium hydroxide solutions are more erratic than those for potassium hydroxide. Extrapolation of these curves

(6) E. C. Nimer, R. E. Hamm and G. C. Lee, *Anal. Chem.*, **22**, 790 (1950).

(7) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950.