THE DISSOCIATION OF POTASSIUM IODIDE AND THE ABSORPTION SPECTRA OF IODINE AND POTASSIUM IODIDE[1]

BY WALLACE R. BRODE

In papers by Brannigan and Macbeth[2] and by Getman,[3] the absorption spectra of inorganic halides have been discussed and data collected especially on the alkali halides. Getman, who confined his experiments to
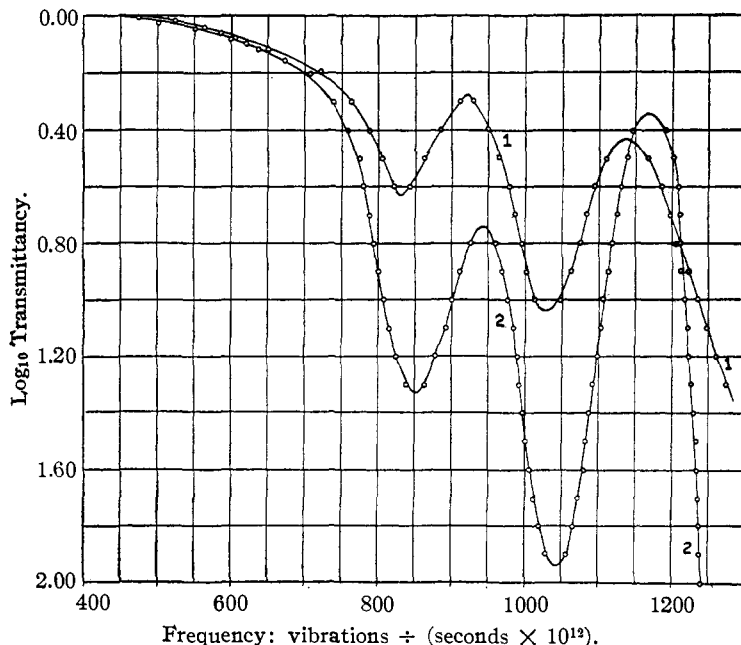

Fig. 1.—The absorption spectrum of iodine in (1) alcohol and (2) potassium iodide solution. Concentration = 0.0003N. Cell thickness = 1 cm. Concentration of KI in potassium iodide solution = 0.125 g. per liter of solution.

various chlorides, showed that with an increase in concentration and an equivalent decrease in cell thickness there was an increase in the extinction coefficient of the band; and since it was assumed that the percentage of ionized chlorine in solution increases with dilution, it was stated that this absorption band could not be due to the free halogen ions. Brannigan and Macbeth performed the same experiments with potassium iodide and drew the same conclusions. In addition they pointed out that the band could

[1] Published by permission of the Director of the National Bureau of Standards of the United States Department of Commerce.

[2] Brannigan and Macbeth, *J. Chem. Soc.*, **109**, 1277 (1916).

[3] Getman, *J. Phys. Chem.*, **29**, 853 (1925).

not, in the case of chlorine, be due to free halogen as the absorption band of this in the form of a gas was at $918f$,[4] whereas the observed absorption band in chloride solutions was at $1119 f$. They did not, however, take into consideration the fact that the absorption band of the halogen in the vapor state might not be the same as in the dissolved state, and in all probability it is not. At least, we do know that iodine does not necessarily give the
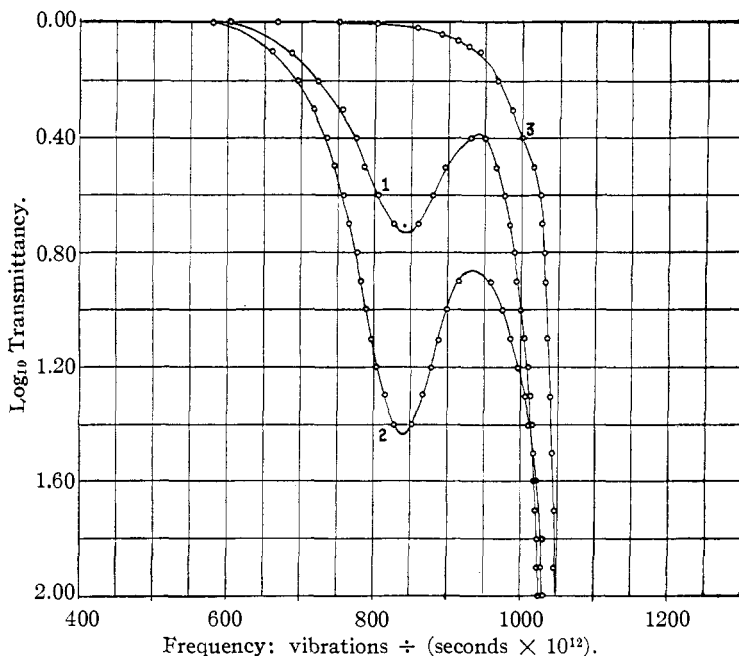

Fig. 2.—(1) The absorption spectrum of a 4 N potassium iodide solution; cell thickness = 4 cm.   (2) The absorption spectrum of a 4 N potassium iodide solution after exposure to north light for three days; cell thickness = 2 cm.   (3) The absorption spectrum of a 4 N potassium iodide solution after the addition of 8 drops of 0.1 N sodium thiosulfate solution to 50 cc. of solution.

same colors in a vapor as in the dissolved state and, as shown by the observations made in this work, the first absorption band in the aqueous solution of iodine in potassium iodide is practically the same in frequency as that determined for the small satellite band observed in a very concentrated solution of potassium iodide. Assuming that this satellite band in the concd. potassium iodide solution is due to free iodine, the amount present may be estimated (approximately, of course, as there must be some solu-

[4] f = vibrations ÷ (seconds × 10^{12}). For a description of the method employed see *Sci. Paper*, **440** (1922) of the Bureau of Standards; Brode, *J. Phys. Chem.*, **30** (1926), or Brode and Adams, THIS JOURNAL, **46**, 2033 (1924), Gibson and others, *J. Optical Soc. Am.*, **10**, 169 (1925).

tion effects), and it was found to be about 0.000383 g. per 100 g. of potassium iodide, or the equivalent in absorption to a 0.0002 N solution of iodine in potassium iodide.

If this band were due to free iodine dissolved in the potassium iodide solution, the addition of a small amount of sodium thiosulfate should completely remove it. Curve 3 of Fig. 2 shows the absorption when a small amount of sodium thiosulfate was added to the potassium iodide solution. The absorption band, so pronounced in Curves 1 and 2, is completely suppressed.
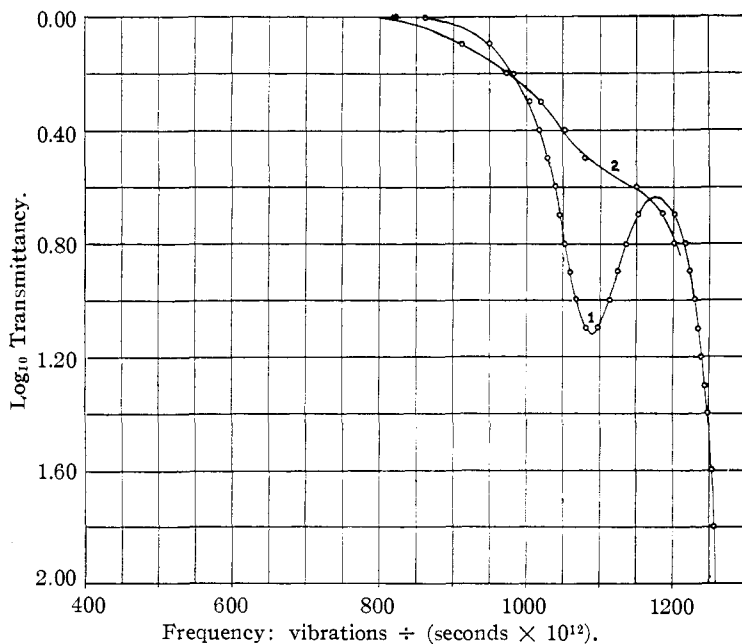

Fig. 3.—(1) The absorption spectrum of a 4 N potassium bromide solution; cell thickness = 4 cm. (2) The same solution after the addition of 8 drops of sodium thiosulfate to 50 cc. of solution; cell thickness = 4 cm.

The same experiment was then tried with a potassium bromide solution with similar effect (Fig. 3). These effects were measured by adding exactly the same amount of sodium thiosulfate to both the halide solution and the comparison solvent so as to eliminate as far as possible any absorption due to the sodium thiosulfate. The sodium thiosulfate absorbed further out in the ultraviolet to such an extent as to prohibit the use of the chloride solutions in this series of experiments.

If this band were due to free iodine and the solution which was known to contain a small amount of dissolved oxygen were exposed to light the amount of iodine in solution should increase. Exposure to north light for three days caused an increase in the extinction coefficient from 0.045 to 0.178 corre-

sponding to nearly four times the amount of free iodine found in the original sample. The frequency and shape of this latter curve were the same as those of the unexposed sample, indicating that the band in both cases was due to the same cause. The addition of sodium thiosulfate to this solution containing the intensified band removed it exactly as before.

The fact that the concentrated solutions of potassium iodide fail to follow Beer's law in regard to this satellite band and that the extinction coefficient actually increases with an increase in the concentration of the potassium iodide in solution does not invalidate the suggestion that this band is due
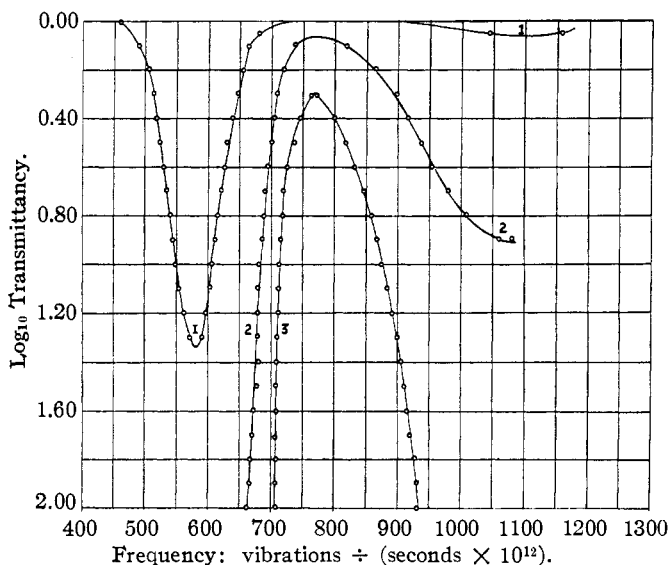

Fig. 4.—The absorption spectrum of iodine in carbon tetrachloride. (1) Concentration = 0.003 N; thickness = 1 cm. (2) Concentration = 0.03 N; thickness = 1 cm. (3) Concentration = 0.03 N; thickness = 4 cm.

to the free halogen. There is little doubt that a reaction of this type which liberates free iodine is promoted by the high concentration of the potassium iodide. With a decrease in the concentration of the potassium iodide one should expect greater stability in the solution and less tendency to liberate free iodine. As indicated by the absorption curves of potassium iodide as compared with that of iodine, there is a strong absorption band characteristic of this salt in the ultraviolet beyond the second iodine band, and it is entirely possible that in the dilute solutions required to observe this band, Beer's law is followed. On the other hand, it is unreasonable to expect solutions of a concentration nearly that of saturation to display dilution effects of a linear order.

The absorption spectrum of iodine in potassium iodide solution exhibits

a higher extinction coefficient and a slightly greater frequency than that of iodine in alcohol. The absorption spectrum of iodine in carbon tetrachloride is similar to the spectrum of iodine in the vapor state, whereas the brown color in the case of alcohol and aqueous potassium iodide solutions indicates that there is some solution effect which as yet is not satisfactorily explained. The fact that the absorption spectra curves of iodine in alcoholic and in aqueous potassium iodide solutions are nearly identical in general shape and frequency range would indicate that the condition of iodine in both of these solutions in certain fundamental respects is the same.
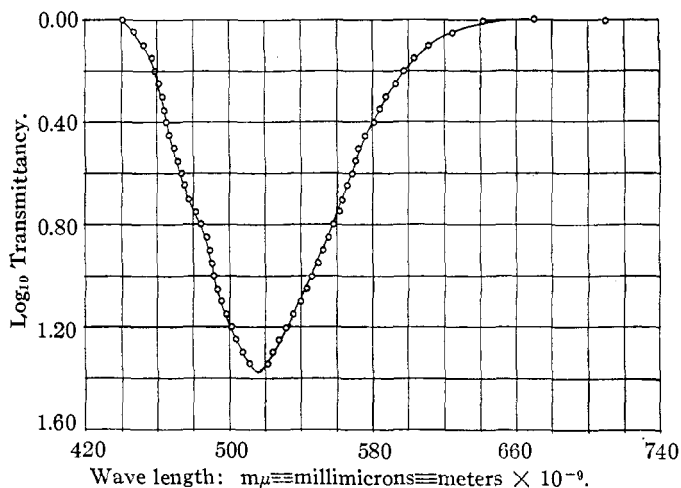

Fig. 5.—The absorption spectrum of iodine in carbon tetrachloride, (visual only). Concentration = 0.0003 N; cell thickness = 10 cm.

The absorption spectrum of iodine in carbon tetrachloride is remarkable for its high transmission in the ultraviolet and were it not for the high volatility of the solvent, such a solution might find considerable use as a light filter to exclude visible light. Care must be taken to make sure that the solvent contains no alcohol or similar impurity as the presence of less than 1% of alcohol will give the alcohol band instead of the carbon tetrachloride band.[5] This is an effect analogous to the effect of alcohol on the absorption spectra of benzene-azophenol in carbon tetrachloride and benzene.[6]

Summary

1. The absorption spectra of iodine have been determined in alcohol, aqueous potassium iodide and carbon tetrachloride.

[5] Lachman, THIS JOURNAL, **25**, 50 (1903). For a complete discussion of the color of iodine solutions see Mellor, "Inorganic and Theoretical Chemistry," Longmans, **1922**, vol. II, p. 110.

[6] Brode, J. Phys. Chem., **30**, 56 (1926).

2. The absorption spectra of potassium iodide have been examined under various conditions and it has been found that the satellite band has the same frequency of vibration as the first band of iodine in a potassium iodide solution and can be completely removed with sodium thiosulfate.

3. It has been shown that this satellite band is due to the presence of free iodine dissolved in a solution of potassium iodide and not to the potassium iodide.

4. The use of iodine dissolved in carbon tetrachloride as a light filter to remove visible light and transmit most of the ultraviolet light to a frequency of 1150 f (the cut-off point of the solvent) has been suggested.

WASHINGTON, D. C.

THE VAPOR PRESSURE OF ANHYDROUS OXALIC ACID

BY W. ALBERT NOYES, JR., AND DELBERT E. WOBBE

In connection with some work on the thermal decomposition of anhydrous oxalic acid[1] it became necessary to know the vapor pressure of anhydrous oxalic acid at temperatures ranging from 120° to 170°. Since anhydrous oxalic acid decomposes quite rapidly in this temperature range it is obvious that direct measurements of the vapor pressure of the anhydrous solid would be very difficult to carry out at these temperatures and that values obtained would be of doubtful accuracy. It seemed advisable to carry out measurements at lower temperatures and to obtain an equation which could be used for purposes of extrapolation.

Some preliminary measurements were made by a static method. Oxalic acid was recrystallized thrice from water and then placed in a flask of about 500cc. capacity sealed to a vacuum line. The flask was surrounded by a salt solution kept at its boiling point (about 105°) and the flask evacuated to as low a pressure as could be obtained with a mercury diffusion pump backed by an efficient oil pump. The evacuation was carried on for 20 to 30 hours. During this time a large portion of the oxalic acid sublimed and condensed along the outlet tube of the flask. The material remaining was usually quite lumpy. The flask was broken off and the outlet covered over with a rubber tip. The lumps were then broken by tapping. The material was kept in a desiccator over phosphorus pentoxide. The preliminary measurements were made by placing some of the anhydrous material in a spiral tube connected with an ordinary manometer. This system was evacuated to as low a pressure as could be obtained with a mercury diffusion pump and was then placed

[1] To be published in the near future.