SPECTROPHOTOMETRIC STUDIES OF BROMINE COMPLEXES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Henry Barber
1958

This is to certify that the

thesis entitled

Spectrophotometric Studies
of
Bromine Complexes

presented by

Henry Barber

has been accepted towards fulfillment
of the requirements for

Ph.D. **degree in** Chemistry

James C. Sternberg
Major professor

Date 15 July 1958

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SPECTROPHOTOMETRIC STUDIES OF BROMINE COMPLEXES

By

Henry Barber

A THESIS

Submitted to the School for Advanced Graduate Studies
of Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1958

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor James C. Sternberg for his guidance and assistance throughout the course of this investigation.

Appreciation is also extended to the Research Corporation for a Frederick Gardner Cottrell grant which provided financial assistance during the academic year 1957-1958.

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AN ABSTRACT

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Year 1958

Approved James C. Sternberg

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ABSTRACT

A spectrophotometric study was undertaken to investigate the nature of complexes involving molecular bromine in solution. Initial studies of the complexing of bromine in aqueous solution were made with the system, water-bromine, which shows, in addition to the visible bromine absorption, a short wavelength band in the approximate wavelength region, 2550-2650Å. These early studies led to the major portion of the present work in which the formation equilibria of the tribromide and dibromochloride ions in aqueous solution at 25° were investigated. Bromine complexing with acetonitrile and ethylene dichloride was also investigated spectrophotometrically.

With the water-bromine system, the interpretation was necessarily qualitative because of the instability, as indicated by the time-dependent spectral changes, of the very dilute bromine solutions. Assuming that the low wavelength band is due principally to the presence of the tribromide ion, which is formed through bromine hydrolysis, a reaction scheme was then postulated to account for the observed changes.

The system, water-bromine-sodium bromide, was ultimately chosen for quantitative study of the tribromide ion equilibrium; formation of the tribromide ion results from the reaction,

$$Br_2 + Br^- = Br_3^-$$

Ultraviolet absorption by the trihalide ion is characterized by a very intense band with a maximum at 2660Å. A method was developed for

treatment of the data, which led to values of 3.46×10^4 and 17.3 liter mole^{-1} for the molar extinction coefficient at the band maximum and the equilibrium constant, respectively. The value for the equilibrium constant is in agreement with those obtained by other investigators using non-spectrophotometric methods based upon distribution experiments.

The dibromochloride ion equilibrium study was first attempted with the system, water-bromine-sodium chloride. However, a complex reaction sequence seemed to prevail, as evidenced by the non-concordant results. It was decided to modify the spectrophotometric approach to the dibromochloride equilibrium by study of the system, water bromine-sodium chloride-sodium bromide; the undesirable effects are suppressed by addition of the bromide. Through use of the data already obtained for the tribromide study, this system did lend itself to quantitative treatment, despite the presence of both the tribromide and dibromochloride ions. The molar extinction coefficient at the band maximum (2430Å) and the equilibrium constant were calculated to be 2.19×10^4 and 1.39 liter mole^{-1}, respectively. The value for the equilibrium constant is in excellent agreement with those resulting from non-spectrophotometric methods.

The system, acetonitrile-bromine, is characterized by an intense ultraviolet absorption with a peak at 2690Å. As with the water-bromine study, a quantitative treatment proved unfeasible due to time-dependent spectral changes. Nevertheless, some significance could be ascribed to the observed changes. The absorption is believed to be due to the ion pair, $CH_3CNBr^{+}Br_3^{-}$. The postulated equilibria for the system, including the formation equilibrium for the ion pair, can lead to an explanation for the spectral changes.

The ethylene dichloride-bromine system also exhibits an intense absorption in the ultraviolet region of the spectrum. The maximum of this band could not be observed because of the limited transparency of the solvent itself. It is probable that the 1:1 complex, $ClCH_2CH_2ClBr_2$, is the absorbing species. The work with ethylene dichloride also led to a novel means for purification of this solvent; the method should prove feasible as a means of obtaining spectroscopic-grade ethylene dichloride.

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INTRODUCTION

Theoretical and spectroscopic considerations suggest an ionic character for certain excited electronic states of aromatic molecules. A study was undertaken to demonstrate, by chemical behaviour, the ionic character of these excited molecules. It was sought to promote a photochemical ring bromination of an aromatic compound containing an aliphatic side chain, through irradiation with wavelengths of ultraviolet light selected to correspond to the appropriate absorption band of the aromatic compound; normal photobromination, in which the actinic radiation is absorbed by the bromine, leads to side-chain bromination of such substituted aromatic compounds through a free-radical mechanism.

A first requirement for the study was an inert solvent, one transparent throughout the ultraviolet region; the high reactivity of bromine seriously complicates the problem of finding such a solvent. The solvents investigated included cyclohexane, ethylene dichloride, and acetonitrile, the latter two being studied the more extensively. While considerable effort was expended, and a novel purification procedure was devised for one of the solvents, ethylene dichloride, the aim of obtaining a suitable one was not achieved. Several fluorocarbon solvents were tried but those readily available were also found to be unsatisfactory.

The use of acetonitrile led to a particularly complicated interaction with bromine, involving initial complexing followed by ion pair formation and dissociation; the system seemed to defy quantitative study.

In an attempt to obtain a simpler prototype for the acetonitrile-bromine system, the trihalide ions in aqueous solution were selected for study. The trihalide study itself has become the major portion of this investigation, and accordingly is presented first in this thesis. The other phases of the study are presented in later sections.

A spectrophotometric study was made of the formation equilibria of the tribromide and dibromochloride ions in aqueous solution. This study has led to a determination of the formation equilibrium constants and molar extinction coefficients for these two trihalide ions. The numerous earlier studies of these trihalide equilibria have, with two exceptions, been based upon distribution experiments rather than spectrophotometric methods, and detailed data on the light absorption characteristics of these ions have been largely lacking; such data are essential to photochemical studies, to theoretical interpretations of the light absorption process (including the nature of the ground and excited states), and to possible analytical applications of spectrophotometric methods to these systems.

The review of past work, and the various phases of this study, will be subdivided according to the apparent complexity of the system. We will first consider the binary system, water-bromine.

PART I

Tribromide and Dibromochloride Ion Formation Equilibria in Aqueous Solution

HISTORICAL SUMMARY

The Water-Bromine System

The ultraviolet absorption spectrum of the system, water-bromine, does not appear to have been interpreted satisfactorily. The following remarks of Bovis (1) seem to be typical of those present throughout the literature:

> Bromine in water exhibits two absorption maxima, one of which lies at 4100Å and the other at 2600Å. Since only the former is exhibited by gaseous and by liquid bromine, the band at 2600Å must be characteristic of bromine in solution.

Figure 1, a spectrum taken from the paper of Katzin (2), shows the visible and ultraviolet absorption of this system. Figure 2, a spectrum also reproduced from the literature (3), represents the absorption of hypobromous acid in water. The latter has been included because of the important role of this acid in the system. The lack of complete interpretation of the spectrum reflects the actual complexity of the system.

The more important of the reactions occurring in an aqueous solution of bromine will now be considered. Bromine hydrolysis proceeds as follows:

$$Br_2 + H_2O = H^+ + Br^- + HOBr \qquad (1)$$

In the presence of light, the hypobromous acid undergoes the decomposition,

$$HOBr + h\nu = H^+ + Br^- + \tfrac{1}{2}O_2 \qquad (2)$$

Besides the photochemical step, the formation of HOBr leads to

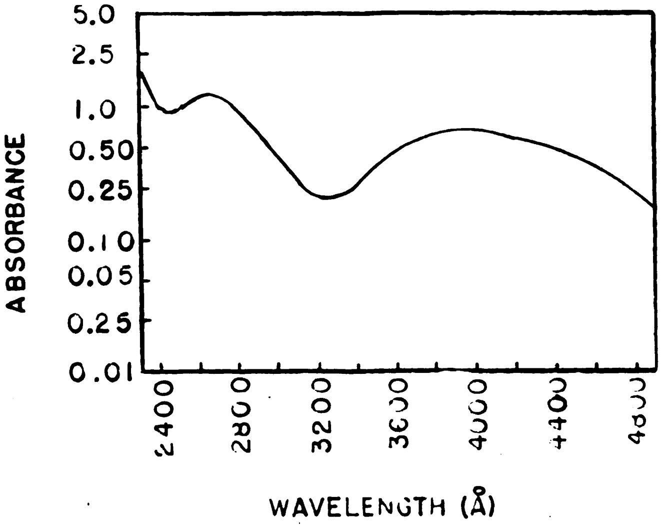


Figure 1. Visible and ultraviolet absorption spectrum of a dilute aqueous solution of bromine (Katzin (2)).

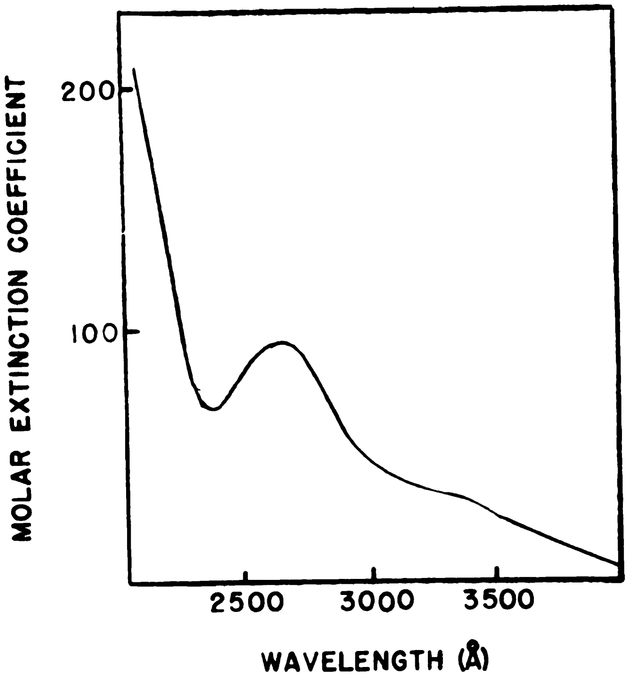


Figure 2. Ultraviolet absorption spectrum of hypobromous acid in aqueous solution (Anbar and Dostrovsky (3)).

additional side reactions. It appears that its decomposition proceeds by two simultaneous, independent paths,

$$5HOBr = H^{+} + BrO_3^{-} + 2H_2O + 2Br_2 \qquad (3)$$

and

$$4HOBr = O_2 + 2H_2O + 2Br_2 \qquad (4)$$

In the dark, reaction (3) predominates. Hypobromous acid is also a very weak acid, its dissociation occurring as follows:

$$HOBr = H^{+} + BrO^{-} \qquad (5)$$

Another reaction which may be significant is the oxidation of hydrobromic acid by bromic acid, i.e.,

$$6H^{+} + 5Br^{-} + BrO_3^{-} = 3Br_2 + 3H_2O \qquad (6)$$

The literature concerning reaction (1), the extensively studied bromine hydrolysis, has been reviewed by Liebhafsky (4); a value of 5.8×10^{-9} for the hydrolysis constant seems to be the most acceptable one. Reaction (2), the photochemical one, has been studied by Pagel and Carlson (5). Reactions (3) and (4) were investigated by Pollak and Doktor (6). Shilov (7) has reported a dissociation constant of $K = 2.06 \times 10^{-9}$ for reaction (5); this value is in good agreement with that of other investigators. Reaction (6) is discussed by Betts and MacKenzie (8). Standard oxidation potentials for reactions (3), (4), and (6) are 0.07, 0.36, and 0.43 volts respectively. These values have been calculated from tabulated half-cell potentials (9). The above oxidation potentials lead to values of 2.59×10, 6.62×10^{5} and 3.08×10^{8} for the respective equilibrium constants.

The addition of bromide ion to the water-bromine system effects considerable simplification, since repression of the hydrolysis reaction virtually eliminates the complex side reactions of hypobromous acid. The system, water-bromine-bromide, is considered next.

The Water-Bromine-Bromide System

The reaction of molecular bromine with bromide ions in aqueous solution yields the anionic donor-acceptor complex, Br_3^-. The formation reaction is as follows:

$$Br_2 + Br^- = Br_3^-$$

With excess bromine, an additional complex Br_5^-, may be formed (10) according to the overall equation,

$$2Br_2 + Br^- = Br_5^-$$

The equilibrium constants for these reactions are:

$$K_3 = \frac{a_{Br_3^-}}{a_{Br_2}\ a_{Br^-}} = \frac{(Br_3^-)}{(Br_2)(Br^-)}\ \frac{f_{Br_3^-}}{f_{Br_2}\ f_{Br^-}}$$

and

$$K_5 = \frac{a_{Br_5^-}}{a^2_{Br_2}\ a_{Br^-}} = \frac{(Br_5^-)}{(Br_2)^2\ (Br^-)}\ \frac{f_{Br_5^-}}{f^2_{Br_2}\ f_{Br^-}}$$

where the quantities in parentheses represent concentrations of the particular species, and the symbols a and f the activities and activity coefficients, respectively. The first of these reactions is the more important, with the extent of the second being relatively negligible under most conditions. In addition, in some studies, the bromine hydrolysis reaction,

$$Br_2 + H_2O = H^+ + Br^- + HOBr$$

must also be considered, although it is appreciably repressed in systems containing added bromide.

Most of the earlier studies of the water-bromine-bromide system were based on a partition or distribution method. By these means, the concentration of free bromine in a solution containing both free bromine and bromide ions is accurately determined after permitting the volatile bromine to reach a state of equilibrium, via the vapor phase, with a similar solution which is, however, free of bromide ions. Since the activity of bromine at equilibrium is the same in both solutions, the concentration of free bromine in the aqueous bromide solution can easily be determined if the activity coefficients are assumed to be the same in both solutions. In the earlier work, activity coefficients were generally neglected, although in several more recent studies they have been included.

The most recent work on the tribromide equilibrium is that of Scaife and Tyrell (11). Here again, a distribution method was applied. It was found advantageous in their work to use a solvent medium of constant acidity and of high and almost constant ionic strength. The slight acidity helped to suppress the hydrolysis reaction and the constant ionic strength to ensure that activity coefficients are independent of changes in concentration of the complex species. These investigators studied the system at three temperatures; 5, 25, and 35° C. Mean values of K_3 for these temperatures were found to be 19.85, 15.53, and 15.28 kg mole^{-1}, respectively (all concentrations were based on the molality scale).

A selection of the best accepted values is shown in the following table, which has been taken from the paper of Scaife and Tyrell.

Salt	Temp. (°C)	K_3(liter mole^{-1})	Source
KBr	0	19.6	(12)
KBr (I = 0.5)*	16.5	18.2	(13)
NaBr (I = 0.5)*	16.5	17.4	(13)
KBr (I = 0.5)*	21.5	17.4	(13)
NaBr (I = 0.5)*	21.5	16.6	(13)
LiBr (I = 0.5)*	21.5	16.2	(13)
KBr	25.0	16.1	(14)
KBr	32.5	15.4	(15)

* I = ionic strength

The only previous spectroscopic studies of the tribromide ion in aqueous solution are those carried out by Gilbert, <u>et al</u>. (16) and Job (17). A number of other trihalide ions, including the dibromochloride (which will be discussed later) were also studied by these workers. Gilbert's group was primarily interested in the general characteristics of the various trihalide spectra in the ultraviolet region, and in possible correlations of spectra and structure. Hydrolysis effects were not considered, and even the well-established trihalide equilibria were not taken into account. For example, in their study of the salt, cesium tribromide, in water, it was assumed that all of the bromine existed as the tribromide ion. The marked changes in observed absorbances with time made quantitative treatment unfeasible. Their data indicate that the tribromide ion absorbs very intensely in the region of 2600Å. Job's work was not complicated by hydrolysis, since he studied the system, water-bromine-potassium bromide. His data did permit calculation of the equilibrium constant; a value of 28.6 liter mole^{-1} resulted (studies were carried out at 16°C). This rather high value can probably be attributed to the experimental means employed by Job. In this early work, which antedated use of the more sensitive photoelectric spectrophotometer, the photographic plate method was used for the detection and recording of the ultraviolet radiation. Popov and Swensen (18) have found that the tribromide ion in ethylene dichloride and acetonitrile also invariably shows a strong absorption in the 2600-2700Å region.

It was considered of interest to study, for purposes of comparison, the interaction of other halide ions with bromine. The only one completed in this study was the system, water-bromine-chloride, discussed in the following section.

The Water-Bromine-Chloride System

The results of previous studies on the dibromochloride equilibrium, $Br_2 + Cl^- = Br_2Cl^-$, in aqueous solution may be summarized as follows: a mean value of 1.39 liter mole^{-1} at 25° C is reported from the data of Jakowkin (19), Dancaster (20), and Ray and Sarkar (21). Jakowkin studied the system, water-bromine-chloride, the chloride being added as the potassium salt. As in the tribromide studies, again a distribution method was used. The other workers used essentially the same procedure. Dancaster's studies included the following salts as a source for the chloride ion: $CuCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CdCl_2$, $HgCl_2$, and $AlCl_3$. The results obtained with each of these salts appeared very self-consistent, with the exception of the chlorides of cadmium and mercury. The study of Ray and Sarkar involved the single system, water-bromine-hydrochloric acid.

Since the distribution method was so widely used for studies of this nature, it may be appropriate to briefly discuss the general calculation procedure. Using the water-bromine-chloride system to illustrate the method, let $\sum Br_2$ be the concentration of titratable bromine in the aqueous phase, $(Br_2)_{CCl_4}$ be the concentration of bromine in the carbon tetrachloride phase, and $\sum Cl^-$ be the total concentration of chloride, i.e., $(Cl^-) + (Br_2Cl^-)$ in the aqueous phase. If D is the distribution constant of the volatile halogen for the water-carbon tetrachloride system, i.e., $D = (Br_2)_{CCl_4}/(Br_2)_{H_2O}$, then the following relationships result:

$$(Br_2)_{H_2O} = (Br_2)_{CCl_4}/D$$
$$(Br_2Cl^-) = \sum Br_2 - (Br_2)_{CCl_4}/D$$
$$(Cl^-) = \sum Cl^- - \sum Br_2 + (Br_2)_{CCl_4}/D$$

The equilibrium constant, K_4, can then be evaluated by substitution of the above quantities into the equilibrium expression,

$$K_4 = \frac{(Br_2Cl^-)}{(Br_2)\ (Cl^-)}$$

The only spectrophotometric investigations of the dibromochloride ion are the previously mentioned studies of Gilbert, et al. (16) and Job (17). For the system, water-bromine-potassium chloride, the former investigators found that an absorption maximum occurred at approximately 2600Å. Extinction coefficients were included in the data, but since the authors themselves attributed little significance to the values, due to the instabilities of the systems, they will not be presented here. Job also studied the particular system, water-bromine-potassium chloride. An equilibrium constant of 0.53 liter mole^{-1} was calculated; the study was carried out at 16°C.

Evaluation of Activity Coefficients

Introduction

It was found necessary, with our calculations, to consider the activity coefficients of the various species involved in each of the different systems studied. The activity coefficients of bromine and, in some instances, of hydrobromic acid, in sodium bromide, sodium chloride, and in mixtures of the two salts were needed. Some background discussion is presented here of the methods and reasoning used for estimation of these quantities.

Bromine in Aqueous Salt Solutions

Numerous studies have been carried out to determine the activity coefficients of non-electrolytes in aqueous salt solutions in which no complexing occurs. It is obvious that direct determination of the activity coefficient of bromine in aqueous sodium bromide cannot be performed because of the formation of the tribromide complex. However, the data compiled from systems free of complexing permit estimation of reasonably accurate values for the activity coefficients of bromine in solutions where complexing does occur. This necessarily indirect method will now be discussed.

A complete survey of the data previous to 1927 by Failey and Randall (22) has demonstrated that a nearly linear relationship exists between the logarithm of the activity coefficient of a given non-electrolyte and the ionic strength of a given aqueous salt solution. Mathematically, this relationship can be expressed as follows:

$$\frac{\log \gamma}{\mu} = \text{constant}$$

The symbols γ and μ represent the molal activity coefficient and the ionic strength (molal scale), respectively. A portion of their data is reproduced in the following table; the values included therein will subsequently be used in our calculations.

Activity Coefficients of Non-electrolytes in Aqueous Salt Solution

Non-electrolyte	Salt	$(\log \gamma)/\mu$	Ratios
N_2O	NaBr	0.091	0.091/0.110 = 0.827
N_2O	Na_2SO_4	0.110	Mean = 0.807
C_2H_2	NaBr	0.077	0.077/0.098 = 0.786
C_2H_2	Na_2SO_4	0.098	
N_2O	NaCl	0.101	0.101/0.110 = 0.918
N_2O	Na_2SO_4	0.110	Mean = 0.934
C_2H_2	NaCl	0.093	0.093/0.098 = 0.949
C_2H_2	Na_2SO_4	0.098	

The significance of the ratios given in the last column of the table will become clear as the discussion proceeds. Theoretical justification for setting up the ratios as shown is given in the paper of Sherrill and Izard (23). Actually, these workers reproduced and elucidated an argument originally proposed by Debye and McAulay (24). The latter had shown, using the results of their ion attraction theory, how the activity coefficient of a non-electrolyte varies, for a given solvent, with the nature and concentration of the non-electrolyte and electrolyte. The derivation of this relationship is complicated; the final result may be expressed for the special case of gas solubility by the relatively simple equation,

$$\log (S_0/S) = K\,(\partial D/\partial S)(1/r)\sum(c_i z_i^2)$$

Here, K is a constant characteristic of the solvent at a temperature T; the ratio, $\partial D/\partial S$, is the rate of change of dielectric constant of the solution (containing only non-electrolyte) with the concentration of the non-electrolyte; r is the mean radius of the ions present; the ratio, S_0/S, is the saturation concentration of non-electrolyte in pure water divided by its value in the presence of the electrolyte; and c_i is the concentration and z_i the charge of any ion of kind i. The ratio, $\partial D/\partial S$, may be assumed to be independent of the concentration, S, and therefore regarded as a constant characteristic of the non-electrolyte. Since the ionic strength, μ, is equal to the quantity, $\frac{1}{2}\sum(c_i z_i^2)$, and the activity, γ, is equal to the ratio, S_0/S, then the relationship above becomes:

$$\frac{\log \gamma}{\mu} = K'(\partial D/\partial S)(1/r) = \text{constant}$$

This equation can be generalized further by expressing it as follows:

$$\frac{\log \gamma}{\mu} = (K_1)(1/r)$$

Thus, K_1 is a constant characteristic of the solvent and non-electrolyte; (1/r) is, of course, characteristic of the salt.

Using the last equation, it will now be shown how some significance can be ascribed to the method used for the calculations:

for bromine in sodium sulfate,

$$(\log \gamma)/\mu = (K_1)_{H_2O \text{ and } Br_2}(1/r)_{Na_2SO_4}$$

for nitrous oxide in sodium sulfate,

$$(\log \gamma)/\mu \;=\; (K_1')_{H_2O\text{ and }N_2O}\;(1/r)_{Na_2SO_4}$$

for nitrous oxide in sodium bromide,

$$(\log \gamma)/\mu \;=\; (K_1')_{H_2O\text{ and }N_2O}\;(1/r)_{NaBr}$$

for bromine in sodium bromide,

$$(\log \gamma)/\mu \;=\; (K_1)_{H_2O\text{ and }Br_2}\;(1/r)_{NaBr}$$

By substitution of the quantities on the right into the expression,

$$\frac{(\log \gamma)/\mu_{\;Br_2\text{ in }Na_2SO_4}\;\;(\log \gamma)/\mu_{\;N_2O\text{ in }NaBr}}{(\log \gamma)/\mu_{\;N_2O\text{ in }Na_2SO_4}}$$

we obtain, by cancellation of like terms, the reduced expression,

$$(K_1)_{H_2O\text{ and }Br_2}\;(1/r)_{NaBr}$$

The latter is identical to the expression desired, i.e., the ratio $(\log \gamma)/\mu$, for bromine in sodium bromide.

Griffith, et al. (13), using the above expressions, calculated the value of $(\log\gamma)/\mu$ for bromine in sodium bromide. The data shown in the preceding table were first supplemented with the corresponding value for bromine in aqueous sodium sulfate. By partition experiments, the partition coefficient for bromine between carbon tetrachloride and an aqueous solution of sodium sulfate (ionic strength = 0.5) was found to be 31.3. Since the partition coefficient of bromine between water and carbon tetrachloride is 27.5, it follows that the activity coefficient of bromine in the sodium sulfate solution is 31.3/27.5 = 1.134. Hence, $(\log \gamma)/\mu = (\log 1.134)/0.5 = 0.109$. It is then inferred, from considerations discussed in the preceding paragraph, that for bromine in sodium bromide, $(\log \gamma)/\mu = 0.109(0.807) = 0.088$. Since the expression, $(\log \gamma)/\mu$, is a constant for a given system, the activity coefficient for bromine in any given solution of sodium bromide can then be easily calculated. For the system, water-bromine-sodium chloride, the ratio was determined in an analogous manner; i.e., $(\log \gamma)/\mu = 0.109(0.934) = 0.102$.

For the mixed salt system studies, the activity of bromine was estimated as follows. From the preceding discussion, it was seen that for bromine in aqueous sodium bromide, the value of $(\log \gamma)/\mu = 0.088$. Similarly, for bromine in aqueous sodium chloride, $(\log \gamma)/\mu = 0.102$. For any mixture of the two salts, it would appear that the $(\log \gamma)/\mu$ value should be closely estimated by the expression,

$$(\log \gamma)/\mu = 0.088 + m' (0.014)$$

The term m' represents the ratio of the molality of sodium chloride to the sum of the molalities of both salts in a given run. The value, 0.014, is the difference in the $(\log \gamma)/\mu$ values for bromine in each of the aqueous salt solutions, i.e., 0.102 - 0.088 = 0.014.

Hydrobromic Acid in Aqueous Sodium Bromide

The activity coefficient of hydrobromic acid in aqueous sodium bromide was calculated from data available in the literature. It was necessary to make two plots of the literature data. For the first, values of the mean ionic activity coefficient of the acid in sodium bromide for a constant acid concentration of 0.01m were plotted versus the concentration of the salt (25). From data of the mean ionic activity coefficient of hydrobromic acid in water (26), a second plot of the mean activity coefficient of the acid versus the concentration of the acid was prepared. By proper interpolation from these two plots, with respect to the individual runs, a third graph was obtained for subsequent use in the calculations. This third graph was drawn for each run. The significance of this latter plot may perhaps be best understood by reference to a particular run. For run 145, the following data are pertinent:

molality of solution = 0.195

$\gamma_{\pm}$ of HBr in H_2O = 0.783
(HBr conc. = 0.195m)

$\gamma_{\pm}$ of HBr in NaBr = 0.769
(0.01m HBr, 0.185m NaBr)

In the plot, the log $\gamma_{\pm}$ for hydrobromic acid was plotted versus the molality of the acid at constant total molality. Extrapolation to zero molality yields a value of $\gamma_{\pm}$ for the acid which should be quite accurate. It will be recalled that the concentration of the acid, formed from the hydrolysis of bromine in aqueous sodium bromide is relatively very low, even in dilute solutions of the salt. This method has been widely used by other investigators. For example, Hawkins (27) has shown that for hydrochloric acid-uniunivalent halide mixtures, this linearity persists at constant total molalities as high as 6 m. Other similar systems have also been studied in this manner.

Hydrobromic Acid in Aqueous Sodium Chloride

The activity coefficient of hydrobromic acid in sodium chloride was calculated from the expression,

$$\gamma_{\pm \text{HBr in NaCl}} = \frac{(\gamma_{\pm \text{HCl in NaCl}})(\gamma_{\pm \text{NaBr in } H_2O})}{(\gamma_{\pm \text{NaCl in } H_2O})}$$

For each calculation, the quantities on the right side of the equation were associated with salt concentrations equal to those for the run under consideration. From the following discussion, it would appear that the above expression should approximate the desired quantity fairly well. Using the definition of mean ionic activity coefficient, the equation can be expressed as follows:

$$\gamma_{\pm \text{HBr in NaCl}} = \frac{(\gamma_{H^+})^{\frac{1}{2}}(\gamma_{Cl^-})^{\frac{1}{2}}(\gamma_{Na^+})^{\frac{1}{2}}(\gamma_{Br^-})^{\frac{1}{2}}}{(\gamma_{Na^+})^{\frac{1}{2}}(\gamma_{Cl^-})^{\frac{1}{2}}}$$

The ionic activity coefficients of the chloride ions can be cancelled from the expression; in the one case (HCl in NaCl), we are choosing the hypothetical, extrapolated condition of zero concentration of acid in the sodium chloride solution--in the other case (NaCl in H_2O), the sodium chloride solution alone is considered. In both instances, the environment of the chloride ion is essentially the same. If one now considers the environment of the sodium ion for the systems, sodium bromide in water and sodium chloride in water, it is clear that a bromide and chloride environment respectively are involved. Assuming that the effect on the sodium ion by the two different species is not appreciably different, we can cancel these terms and arrive at the following:

$$\gamma_{\pm \mathrm{HBr\ in\ NaCl}} = (\gamma_{\mathrm{H}^+})^{\frac{1}{2}} (\gamma_{\mathrm{Br}^-})^{\frac{1}{2}}$$

The expression on the right side is, by definition, the mean ionic activity coefficient of the hydrobromic acid. For a given run, the value of $\gamma_{\pm \mathrm{HCl\ in\ NaCl}}$ was calculated in the same manner as was the coefficient for hydrobromic acid in sodium bromide (preceding section). The values for the mean ionic activity coefficients of the sodium bromide and sodium chloride in water were taken from the literature (28).

Conversion of Activity Coefficients

With all subsequent calculations, it will be noted that concentrations are expressed in terms of molarities. Since the literature data used for activity coefficient calculations are based on the molality scale (as discussed in the preceding pages), it was necessary to convert all activity coefficients. The conversion was made by use of the formula (29), $f_{\pm} = (1 + 0.001mW_B)(d_0/d)\,\gamma_{\pm}$, where the quantities are defined as follows:

$f_{\pm}$ = mean molar ionic activity coefficient

m = molality of solution

W_B = molecular weight of the solute

d_0 = density of the solvent

d = density of the solution

$\gamma_{\pm}$ = mean molal ionic activity coefficient

The analogous formula, $f = (1 + 0.001 m W_B)(d_0/d)\gamma$, was employed for conversions involving the non-electrolyte, bromine. For the case of a mixed electrolyte, the extended formula, $f_{\pm} = (1 + 0.001 \sum m W_B)(d_0/d)\gamma_{\pm}$, was used for converting from the molal to the molar scale (29).

THE PRESENT INVESTIGATION--RESULTS AND DISCUSSION

The various systems studied in this investigation are the following: water-bromine, water-bromine-bromide, water-bromine-chloride, and water-bromine-chloride-bromide. Each of these will now be considered in some detail.

The Water-Bromine System

The water-bromine system was initially studied in an attempt to elucidate the origin of the short wavelength band in the ultraviolet region of the spectrum. Our studies clearly demonstrate that this band can be ascribed to the presence of the tribromide ion, which results simply from the reaction of molecular bromine with the bromide ions formed in the hydrolysis step, i.e.,

$$H_2O + Br_2 = HOBr + H^+ + Br^-$$

$$Br_2 + Br^- = Br_3^-$$

In an attempt to verify this interpretation quantitatively, a study was planned in which both reactions, the hydrolysis and the tribromide formation equilibria, would be accounted for in the mathematical treatment of the data. Unfortunately, however, quantitative treatment was not possible because of the spectral changes which occurred with time.

When no precautions were taken to exclude light, the intensity of the absorption maximum in the 2550 to 2650Å region always showed a definite increase with an accompanying shift to longer wavelengths. A typical increase would amount to approximately one-tenth of an absorbance unit; the shift would be of the order of five angstroms. A period of several hours was usually necessary for these changes to occur. This instability made quantitative treatment impossible. Figure 3, a typical spectrum for the system, illustrates the observed trends. Two 200-watt tungsten lamps, placed several feet from the absorption cell during the exposure periods, were used as light sources.

The changes mentioned above could be accounted for by the subsequent behaviour of the hypobromous acid which is formed in the hydrolysis. Hypobromous acid readily undergoes decomposition in one of two ways. In the presence of light, the decomposition proceeds largely in accordance with the following reaction [reaction (2), early discussion]:

$$2HOBr = 2H^+ + 2Br^- + O_2$$

The bromide ion formed enters into the tribromide equilibrium, thus increasing the tribromide ion concentration. Therefore, because of the intense absorption of light by the tribromide ion, even a very small change in its concentration would result in an appreciable change in the absorption spectrum. The shift may be explained by the depletion of the hypobromous acid together with the accompanying increase in the tribromide ion. Anbar and Dostrovsky (3) and other independent workers have studied the ultraviolet absorption of hypobromous acid in aqueous solution (Figure 2). The acid has two absorption maxima, one at 2600 and the other at 3200Å. The short and long bands have molar extinction values of approximately 95 and 35 liter mole^{-1} cm^{-1} respectively. Since the tribromide absorption maximum occurs at 2660Å, the observed wavelength shift could thus be explained.

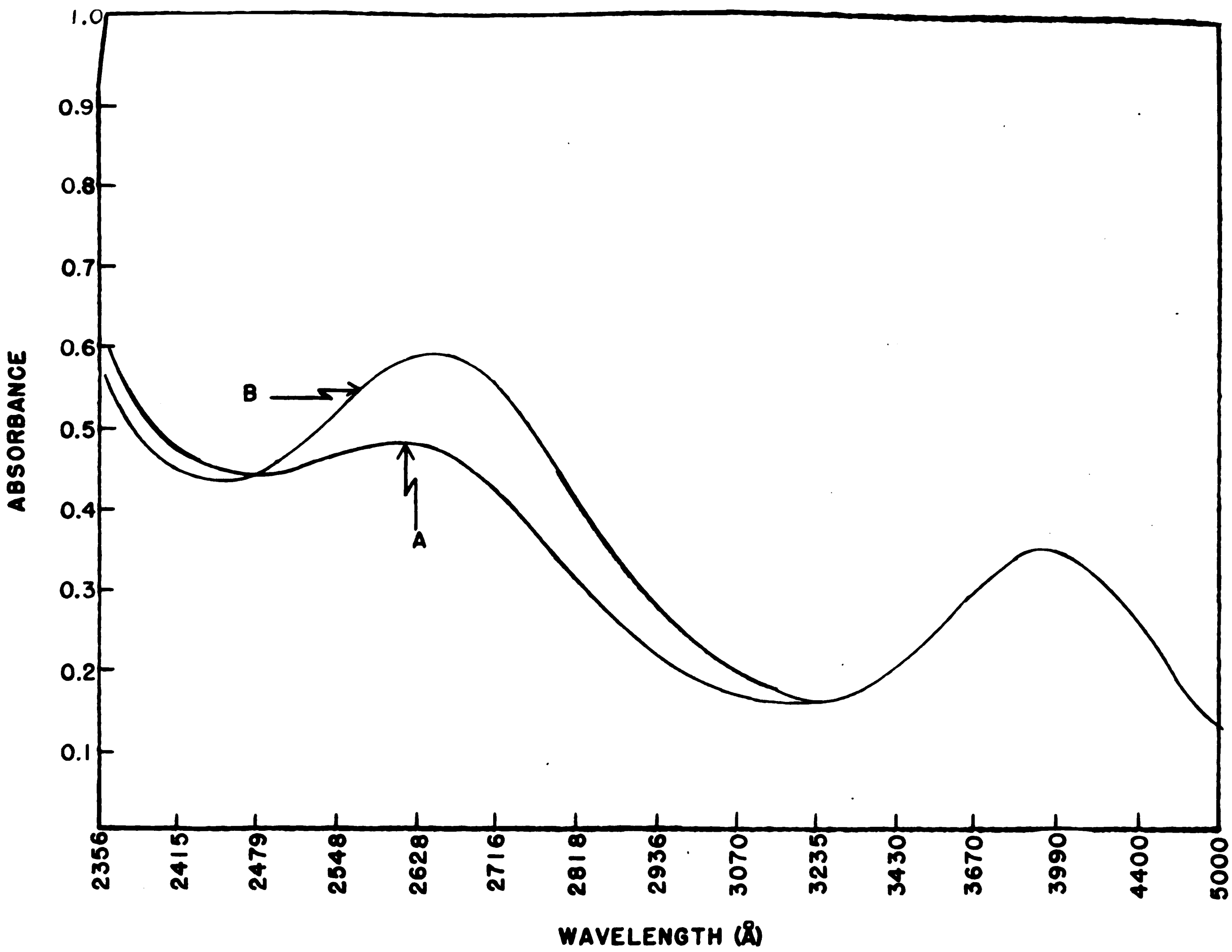


Figure 3. Effect of light on the ultraviolet absorption of a dilute aqueous solution of bromine. Spectrum A was obtained immediately after preparation of the solution; spectrum B was recorded six hours later. The concentration of bromine is approximately 2 x 10^{-3} molar.

When precautions were taken to exclude light, it was observed that again a time-dependent shift to longer wavelengths occurred in the 2550 to 2665Å region. Under these conditions, however, the absorption maximum decreased in intensity. An accompanying slight increase in the bromine band intensity at 3900Å was also noted. The magnitudes of the changes for the short wavelength band were approximately the same as for the case discussed in the preceding paragraph. Typical spectra for this system are shown in Figure 4.

Since even the "dark" system displayed instability, no reproducible quantitative results were obtained, and any explanation of the behaviour must be speculative. The following combination of effects seems consistent with the earlier discussion and is capable of explaining the observed trends. If the tribromide ion is indeed the main contributor to the short wavelength band, then since this band decreases in intensity, while the bromine band intensity at 3900Å undergoes an increase, it follows that the bromide ion concentration must decrease. The shifting of the short wavelength band to longer wavelengths also indicates a lowering of the hypobromous acid concentration, so that the hydrogen ion concentration must increase to maintain the hydrolysis equilibrium. From a consideration of the important reactions, one might arrive at the following explanation for the observed spectral changes. Hypobromous acid would, of course, be produced in the hydrolysis step. Its decomposition in the dark could then proceed as shown by reaction (3), i.e.,

$$5HOBr = H^+ + BrO_3^- + 2Br_2 + 2H_2O \qquad (3)$$

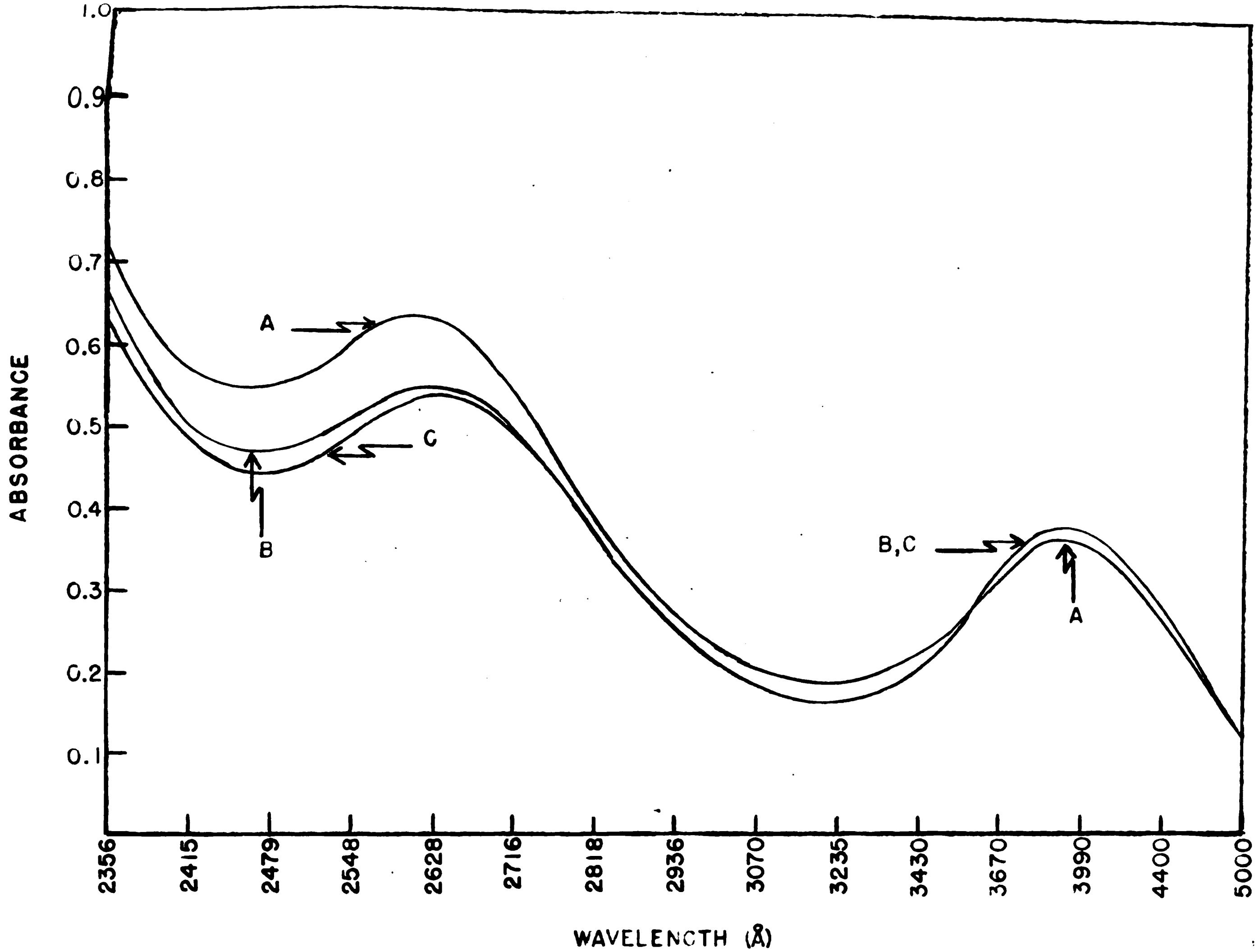


Figure 4. Ultraviolet spectral changes exhibited by a dilute aqueous solution of bromine when light is excluded from the system. Spectrum **A** was obtained immediately after preparation of the solution; spectra B and C were recorded four and seven hours later respectively. The concentration of bromine is approximately 2×10^{-3} molar.

Subsequent oxidation of hydrobromic acid would then occur according to reaction (6).

$$6H^+ + 5Br^- + BrO_3^- = 3Br_2 + 3H_2O \qquad (6)$$

If all of the bromic acid produced by (3) were not consumed in (6), the conditions stipulated above would be satisfied. The hydrogen ion concentration would increase, that of the bromide decrease, that of the hypobromous acid decrease, and that of the free bromine increase. Reactions (2) and (4) need not be considered since their occurrence requires the presence of light. The ionization of hypobromous acid can also be overlooked; the dissociation constant is so small that the concentrations of the ionization products would be insignificant. From the known chemistry of bromine and its acids, this explanation seems to be a reasonable one.

One of our runs was initially studied in the "light" and then followed in the "dark." The interesting results are shown in Figure 5. It is seen that the changes are precisely what one might predict from the "light" and "dark" reactions discussed separately above. The short wavelength band first increased in intensity with an accompanying shift to longer wavelengths. When light was later excluded from the system, this same band decreased in intensity with the shift toward longer wavelengths again occurring. In addition, the bromine band was observed to show a slight increase during the "dark" stage of the study.

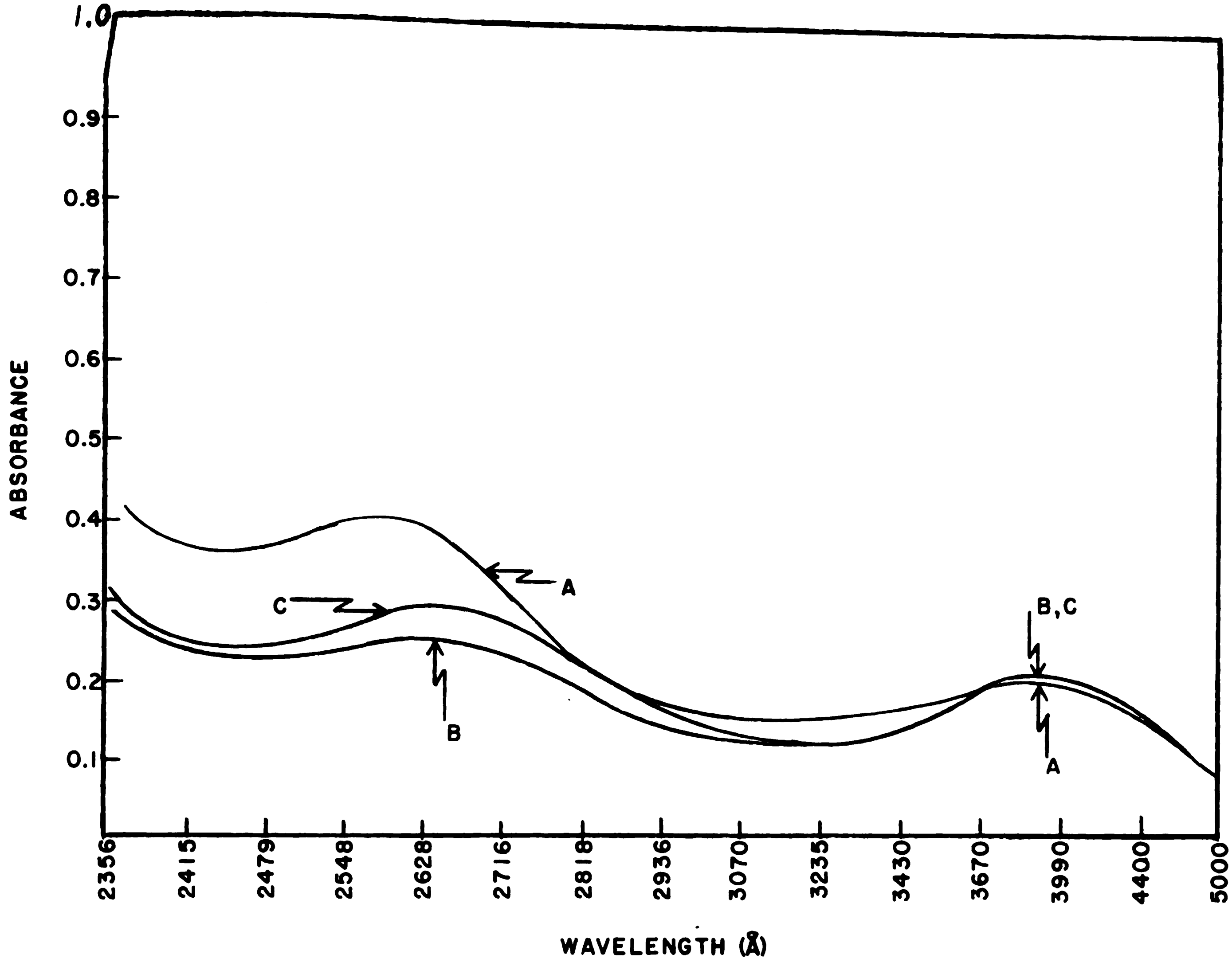
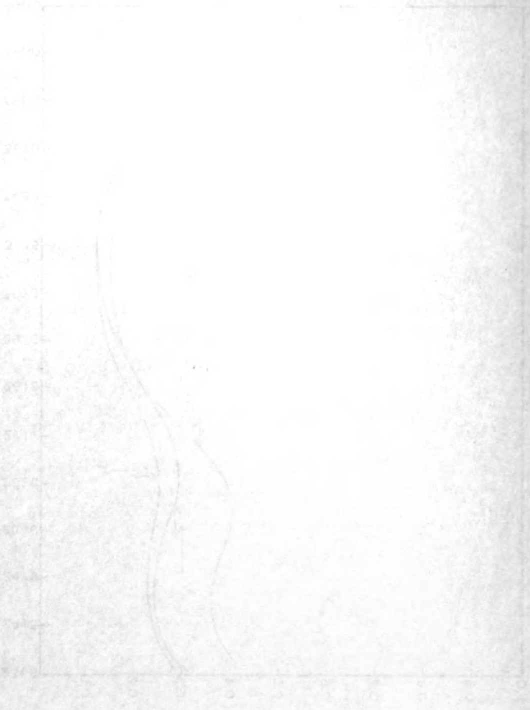


Figure 5. Ultraviolet spectral changes exhibited by a dilute aqueous solution of bromine when system is first studied in the "light" and then in the "dark". Spectra A and B are concerned with the "dark" study; A was obtained immediately after preparation of the solution and B recorded nine hours later. Spectrum C shows the effect of three hours of light exposure. The concentration of bromine is approximately 1 x 10^{-3} molar.



The Water--Bromine-Sodium Bromide System

The instability in the above system was eliminated in the next phase of our study by the addition of sodium bromide, which suppresses the hydrolysis. Runs 138-140 and 142-152 were concerned with this portion of our work. The spectra obtained verified the anticipated stability; absorption readings for any one run at a given wavelength were virtually constant with time in all cases. The observed absorption maxima occurred at 2660Å in these runs, indicating no contribution from hypobromous acid. A typical spectrum is shown in Figure 6.

Determination of e_{2660} - Hydrolysis Neglected (Method 1)

Various methods of treating the data were employed. The expressions used in the first method will now be derived. Consider the following equilibrium:

$$Br_2 + Br^- = Br_3^-$$

Let a be the initial concentration of bromine, b the initial concentration of bromide, y the equilibrium concentration of the tribromide ion, f_{Br_2} the activity coefficient of bromine, and $f_{Br_3^-}$ and f_{Br^-} the activity coefficients of the tribromide and bromide ions respectively. Then,

$$K_3 = \frac{y}{(f_{Br_2})(a - y)(b - y)} \cdot \frac{(f_{Br_3^-})}{(f_{Br^-})}$$

Neglecting the y term relative to b, and assuming the ratio, $(f_{Br_3^-})/(f_{Br^-})$, to be essentially unity, we get

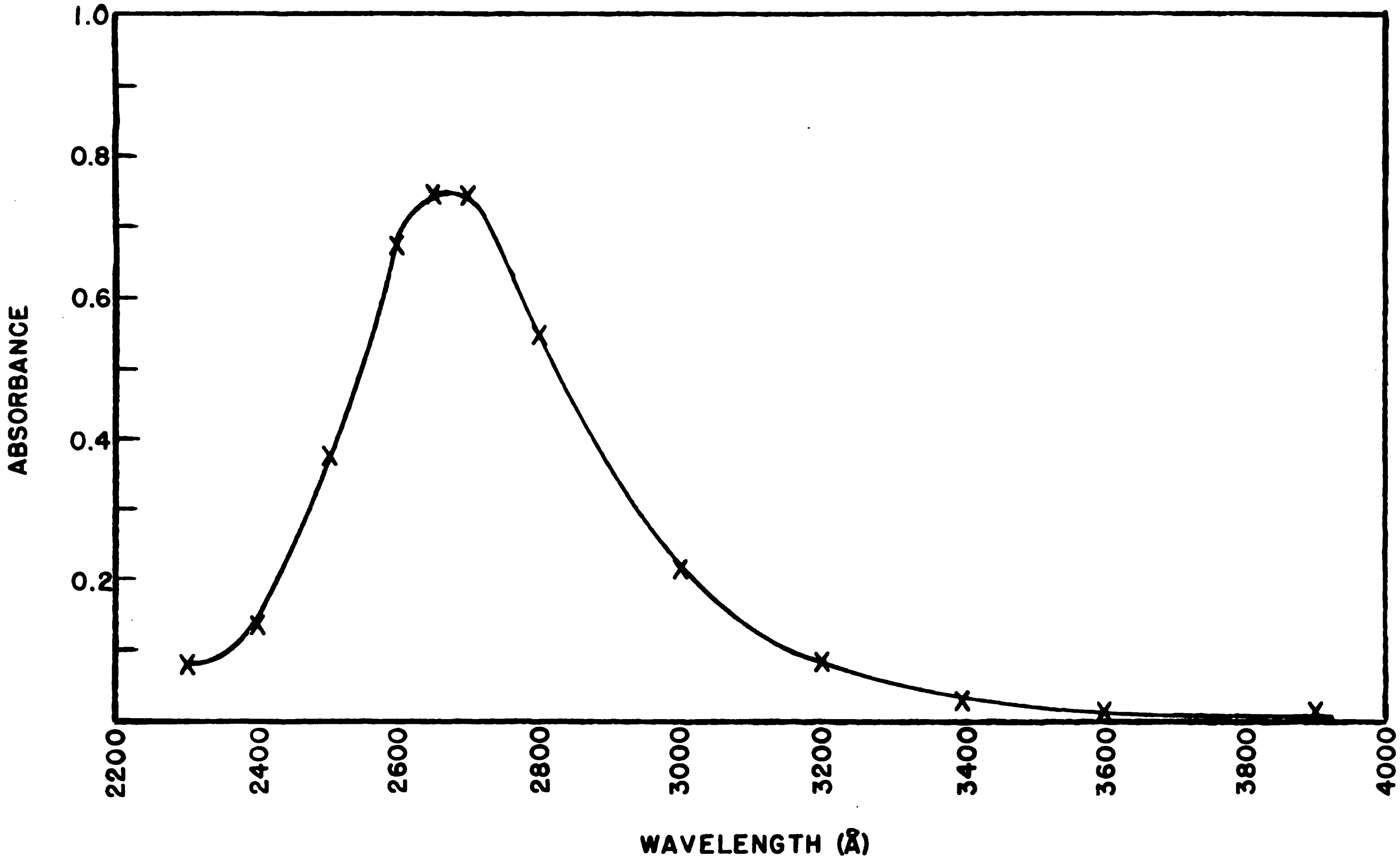


Figure 6. Ultraviolet absorption spectrum of the H_2O-Br_2-NaBr system at 25°C. The concentration of the bromine is 3.68×10^{-4} molar. The concentration of the sodium bromide is 8.598×10^{-2} molar. (Run 144)

$$K_3 = \frac{y}{(f_{Br_2})(a - y)b} = \frac{y}{(f_{Br_2})(ab - by)}$$

Solving for y gives

$$y = \frac{K_3ab(f_{Br_2})}{1 + K_3b(f_{Br_2})}$$

The justification for neglecting the y term relative to b can be seen from a consideration of the relative concentration values of a and b (Table 1). In most of the runs, b is more than a hundredfold greater than a. Since y is necessarily less than a, the difference between b and y is even greater than between b and a. Using a value of $K_3 = 17$ liter mole^{-1}, the tribromide ion concentration was calculated for each run from the data. The value, $K_3 = 17$ liter mole^{-1}, is representative of those in the literature (11). The molar extinction coefficient, e_{2660}, was then calculated from the expression, $e = A/yl$, where A is the observed absorbance and l is the path length of the quartz cell used in the studies. Table 1 shows the results of these calculations.

Determination of e_{2660} - Hydrolysis Considered (Method 2)

A second and somewhat lengthier method of treating the data included the effect of hydrolysis. Let a, b, and y represent the same quantities as before. The two equilibria,

$$H_2O + Br_2 = HOBr + H^+ + Br^-$$

and

$$Br_2 + Br^- = Br_3^-$$

TABLE I

DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENT, e_{2660}, FOR TRIBROMIDE ION HYDROLYSIS NEGLECTED

(Value of $K_3 = 17$ Used in Calculations)**

Run Number	Initial Br_2 Conc. (a) (moles/liter) (x 10^4)	Initial NaBr Conc. (b) (moles/liter) (x 10^2)	Br_2 Activity Coef. (f)*	Absorbance (A) at 2660Å (1 mm. light path)	Equil. Br_3^- Conc. (y) (moles/liter) (x 10^4)	Molar Ext. Coef. (e_{2660}) (liter/mole/cm.) (x 10^{-4})
138	2.94	0.9623	1.002	0.145	0.415	3.50
139	3.88	1.371	1.003	0.265	0.735	3.60
140	6.74	3.051	1.007	0.748	2.31	3.24
142	4.71	4.386	1.009	0.651	2.02	3.22
143	4.24	4.574	1.011	0.632	1.86	3.39
144	3.68	8.598	1.019	0.752	2.20	3.41
145	3.86	19.40	1.045	1.03	2.99	3.44
146	3.85	40.21	1.095	1.22	3.40	3.59
147	3.87	82.50	1.211	1.28	3.65	3.50
148	3.84	110.8	1.296	1.21	3.69	3.28
149	4.01	69.72	1.172	1.31	3.74	3.50
150	4.11	106.4	1.279	1.43	3.94	3.63
151	3.94	214.7	1.679	1.38	3.88	3.56
152	3.86	418.7	2.638	1.28	3.84	3.33
						Mean = 3.44

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* ($f = f_{Br_2}$)

** Representative of those in literature (11).

are now considered. If x is the concentration of the bromide ion produced from the hydrolysis, the equilibrium expressions become

$$K_h = \frac{x^2(b + x - y)}{(a - x - y)} \cdot \frac{(f_{H^+})(f_{HOBr})(f_{Br^-})}{(f_{Br_2})}$$

and (again assuming $f_{Br_3^-} = f_{Br^-}$),

$$K_3 = \frac{y}{(f_{Br_2})(a - x - y)(b + x - y)}$$

Then assuming further that $f_{HOBr} = f_{Br_2}$, since these are both neutral species, the ratio of the equilibrium constants gives

$$K_h/K_3 = \frac{x^2(b + x - y)^2}{y} \; (f_{H^+})(f_{Br^-})(f_{Br_2})$$

$$= \frac{x^2(b + x - y)^2}{y} \; (f_{\pm HBr})^2(f_{Br_2})$$

and

$$(K_h/K_3)^{\frac{1}{2}} = \frac{x(b + x - y)}{y^{\frac{1}{2}}} \; (f_{\pm HBr})(f_{Br_2})^{\frac{1}{2}}$$

Rearrangement of terms gives

$$x^2 + x(b - y) = \frac{(K_h/K_3)^{\frac{1}{2}} y^{\frac{1}{2}}}{(f_{\pm HBr})(f_{Br_2})^{\frac{1}{2}}} \qquad (1)$$

Again assuming $f_{Br_2} = f_{HOBr}$, the product of the equilibrium constants gives

$$K_h K_3 = \frac{x^2 y}{(a - x - y)^2} \; \frac{(f_{H^+})(f_{Br^-})}{(f_{Br_2})}$$

$$= \frac{x^2 y}{(a - x - y)^2} \; \frac{(f_{\pm HBr})^2}{(f_{Br_2})}$$

and

$$(K_hK_3)^{\frac{1}{2}} = \frac{xy^{\frac{1}{2}}}{(a - x - y)} \frac{(f_{\pm HBr})}{(f_{Br_2})^{\frac{1}{2}}}$$

Solving for x,

$$x = \frac{(K_hK_3)^{\frac{1}{2}}(a - y)}{\frac{y^{\frac{1}{2}}(f_{\pm HBr})}{(f_{Br_2})^{\frac{1}{2}}} + (K_hK_3)^{\frac{1}{2}}} \qquad (2)$$

Equations (1) and (2) were solved for x by choosing arbitrary values for y. When x is plotted versus y for each equation, the point of intersection of the two curves obtained gives the values of x and y consistent with the two equilibria for the system. This procedure was followed for each run. The results of these calculations are shown in Table II.

Because of the very dilute salt solutions used for runs 138 and 139, the usual method for determining the mean ionic activity coefficient of the hydrobromic acid was not possible; i.e., the literature data did not extend into this very dilute range. Calculations for the two runs were made with the assumption that the activity coefficient was equal to unity. Runs above 146 were not analyzed according to this method. With these later runs, hydrolysis effects were insignificant, and the method is reduced to the one used in the preceding section. The very small discrepancy between the results obtained by the first and second methods, as seen from a comparison of Tables I and II, indicates that the hydrolysis equilibrium can be neglected in all runs with added bromide.

TABLE II

DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENT, e_{2660}, FOR TRIBROMIDE ION HYDROLYSIS CONSIDERED

(Values of K_3 = 17 and K_h = 5.8 x 10^{-8} Used in Calculations)**

Run No.	Initial Br_2 Conc.(a) (moles/liter) (x 10^4)	Initial NaBr Conc. (b) (moles/liter) (x 10^2)	Activity Coef. Br_2(f)	Activity Coef. HBr($f_\pm$)*	Absorbance (A) at 2660Å (1 mm. light path)	Equil. Br_3^- Conc.(y) (moles/liter) (x 10^4)	Extent of Hydrolysis(x) (moles/liter) (x 10^6)	Molar Ext. Coef.(e_{2660}) (liter/mole/cm.) (x 10^{-4})
138	2.94	0.9623	1.002	~1	0.145	0.397	12.1	3.65
139	3.88	1.371	1.003	~1	0.265	0.741	11.4	3.71
140	6.74	3.051	1.007	0.857	0.748	2.25	10.8	3.32
142	4.71	4.386	1.009	0.834	0.651	2.01	7.03	3.25
143	4.24	4.574	1.011	0.832	0.632	1.88	6.38	3.37
144	3.68	8.598	1.019	0.804	0.752	2.18	3.93	3.46
145	3.86	19.40	1.045	0.771	1.03	3.01	3.01	3.42
146	3.85	40.21	1.095	0.762	1.22	3.45	~1	3.54
								Mean = 3.47

* $f = f_{Br_2}$ and $f_\pm = f_{\pm Hbr}$

** Representative of those in literature (4,11).

Determination of K_3 and e_{2660} (Method 3)

A third method of calculation was tried in which both K_3 and e_{2660} were calculated. The fact that K_3 was evaluated by this method probably makes it the most desirable of the three. In this case the hydrolysis reaction was neglected, as was shown to be justified by the previous calculations, because of the direct suppression of the hydrolysis by the added bromide. Development of the expression used in the calculations proceeds as follows:

Considering only the tribromide equilibrium,

$$Br_2 + Br^- = Br_3^-$$

and

$$K_3 = \frac{y}{(f_{Br_2})(a - y)(b - y)}$$

where a, b, and y are the concentrations of bromine, bromide, and tribromide, respectively, as in the previous methods. Since b is much greater than y in the runs where bromide has been added, the equation becomes

$$K_3 = \frac{y}{(f_{Br_2})(a - y)b}$$

By rearrangement and substitution of the value A/el for y, the concentration of Br_3^-,

$$abl(f_{Br_2})/A = 1/K_3e + b(f_{Br_2})/e$$

Therefore, a plot of $abl(f_{Br_2})/A$ versus $b(f_{Br_2})$ should yield a straight line with intercept equal to $1/K_3e$ and slope equal to $1/e$. Figure 7 shows this plot. A least squares analysis of the data resulted in

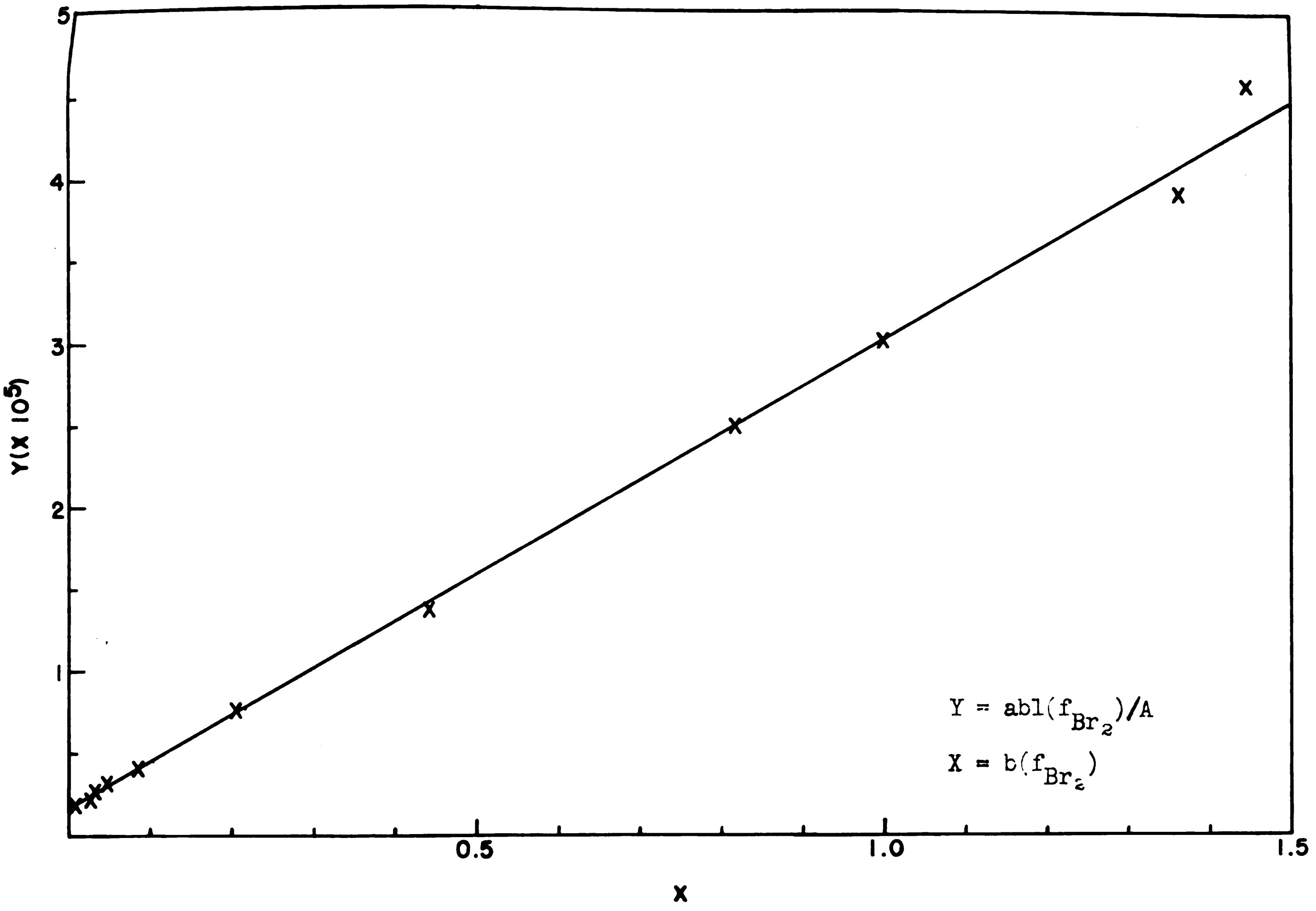

Figure 7. Test of the linear relationship used for determination of the formation equilibrium constant, K_3, and the molar extinction coefficient, e_{2660}, for tribromide ion. (Values plotted listed in Table III.)

values of 17.3 liter mole^{-1} and 3.46×10^4 for K_3 and e_{2660}, respectively. Table III includes the values used for the least squares treatment.

The excellent agreement between these spectrophotometric results and the results of earlier distribution studies verifies the identity of the band at 2660Å as due to the tribromide ion and affords, for this ion, a value for the molar extinction coefficient which can be utilized as an analytical tool in any further studies.*

The Water-Bromine-Sodium Chloride System

Determination of K_4 and e_{2380} - Hydrolysis Neglected (Method 1)

The first series of runs in regard to the dibromochloride ion were studied in the system, water-bromine-sodium chloride. Although hydrolysis in this system is not directly suppressed, as was the case with the system, water-bromine-bromide, it should nevertheless be diminished appreciably because of the reduction in bromine concentration through the dibromochloride equilibrium. The first set of calculations were therefore made with the assumption that the hydrolysis effects could be neglected. It was also necessary to assume (analogous to the assumption, $f_{Br_3^-} = f_{Br^-}$, made for the tribromide ion study) that $f_{Br_2Cl^-} = f_{Cl^-}$. Preliminary studies had indicated that the

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*Using the triiodide absorption maximum at 3520Å, Custer and Natelson (31) have made spectrophotometric determinations of microquantities of iodine. A 5% KI solvent was utilized for complexing of the iodine. As little as 0.2 micro grams of iodine per milliliter could be determined.

TABLE III

DETERMINATION OF THE FORMATION EQUILIBRIUM CONSTANT, K_3, AND THE MOLAR EXTINCTION COEFFICIENT, e_{2660}, FOR TRIBROMIDE ION

(Data Used in Least Squares Treatment)

Run No.	Initial Br_2 Conc.(a) (moles/liter) (x 10^4)	Initial NaBr Conc.(b) (moles/liter) (x 10^2)	Br_2 Activity Coef.(f)*	Absorbance(A) at 2660Å (1 mm. light path)	X = bf* (x 10^2)	Y = ablf/A* (x 10^6)	XY (x 10^7)	X^2 (x 10^3)
138	2.94	0.9623	1.002	0.145	0.9645	1.958	0.1888	0.09303
139	3.88	1.371	1.003	0.265	1.375	2.013	0.2768	0.1891
140	6.74	3.051	1.007	0.748	3.073	2.768	0.8504	0.9442
142	4.71	4.386	1.009	0.651	4.427	3.203	1.418	1.960
143	4.24	4.574	1.011	0.632	4.622	3.098	1.432	2.137
144	3.68	8.598	1.019	0.752	8.764	4.290	3.760	7.681
145	3.86	19.40	1.045	1.03	20.27	7.593	15.39	41.09
146	3.85	40.21	1.095	1.22	44.02	13.91	61.22	193.8
147	3.87	82.50	1.211	1.28	99.92	30.20	301.8	998.3
148	3.84	110.8	1.296	1.21	143.6	45.52	653.5	2061
149	4.01	69.72	1.172	1.31	81.74	25.01	204.5	668.1
150	4.11	106.4	1.279	1.43	136.1	39.07	531.7	1852

* $f = f_{Br_2}$

$\sum X = 5.488$

$\sum Y = 1.786 \times 10^{-4}$

$\sum XY = 1.776 \times 10^{-4}$

$\sum X^2 = 5.827$

Results of Least Squares Analysis:

Intercept = 1.670×10^{-6}

Slope = 2.890×10^{-5}

e_{2660} = 1/slope = 3.46×10^4

K_3 = 1/(intercept)(e_{2660}) = 17.3 liter $mole^{-1}$

absorption maximum of the dibromochloride ion is located at approximately 2380Å (Figure 8). The method of calculation was equivalent to the last of the three used for the tribromide study. Here a plot of $acl(f_{Br_2})/A$ versus $c(f_{Br_2})$ was made (Figure 9), in which the concentration of chloride ion, c, has replaced the concentration of bromide ion, b, used in the previous study. A least squares method was used to obtain values of 0.567 liter $mole^{-1}$ and 3.47×10^4 for K_4 and e_{2380}, respectively (K_4 will represent the equilibrium constant for the present system). Tabulation of the data and the values used in the least squares treatment are shown in Table IV. While a linear relationship appears to hold approximately, the scatter of results is well outside the experimental errors (as seen by the excellent linearity obtained in the tribromide system), and it appears possible that even the approximate linearity in this treatment is fortuitous. Furthermore, there is a considerable disparity in our values of the equilibrium constant relative to the approximate value of 1.40 reported separately by Jakowkin (19), Dancaster (20), and Ray and Sarkar (21) on the basis of distribution experiments; it is apparent that the results obtained by these earlier workers cannot be lightly dismissed, particularly when our results do not show the desired internal consistency. Thus another method of treatment of the data was attempted.

Determination of K_4 and e_{2380} - Hydrolysis Considered (Method 2)

The second method of calculation will now be discussed. Since no bromide was added to the system, hydrolysis seemed a likely source of

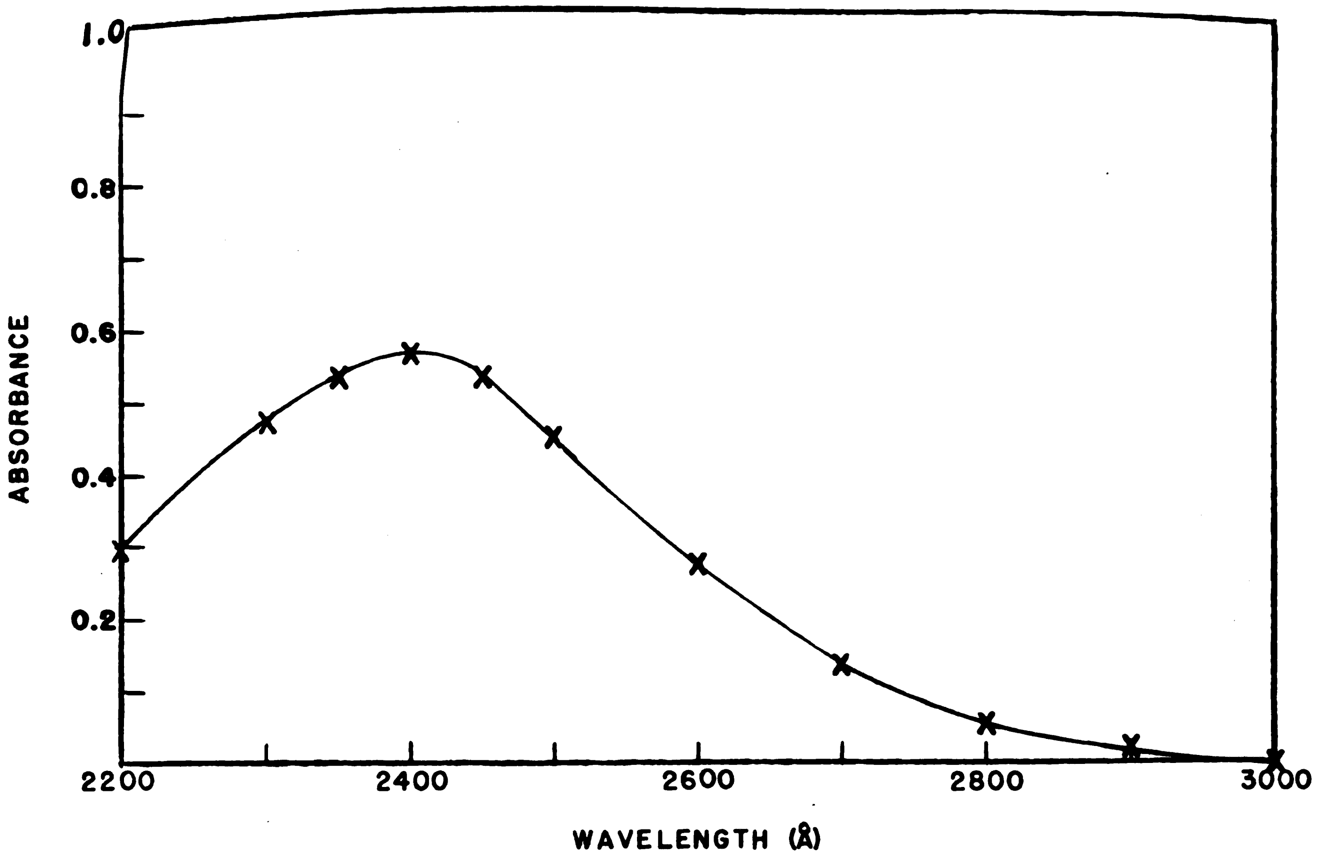


Figure 8. Ultraviolet absorption spectrum of the H_2O-Br_2-NaCl system at 25°C. The concentration of the bromine is 8.75×10^{-4} molar. The concentration of the sodium chloride is 0.4183 molar. (Run 162)

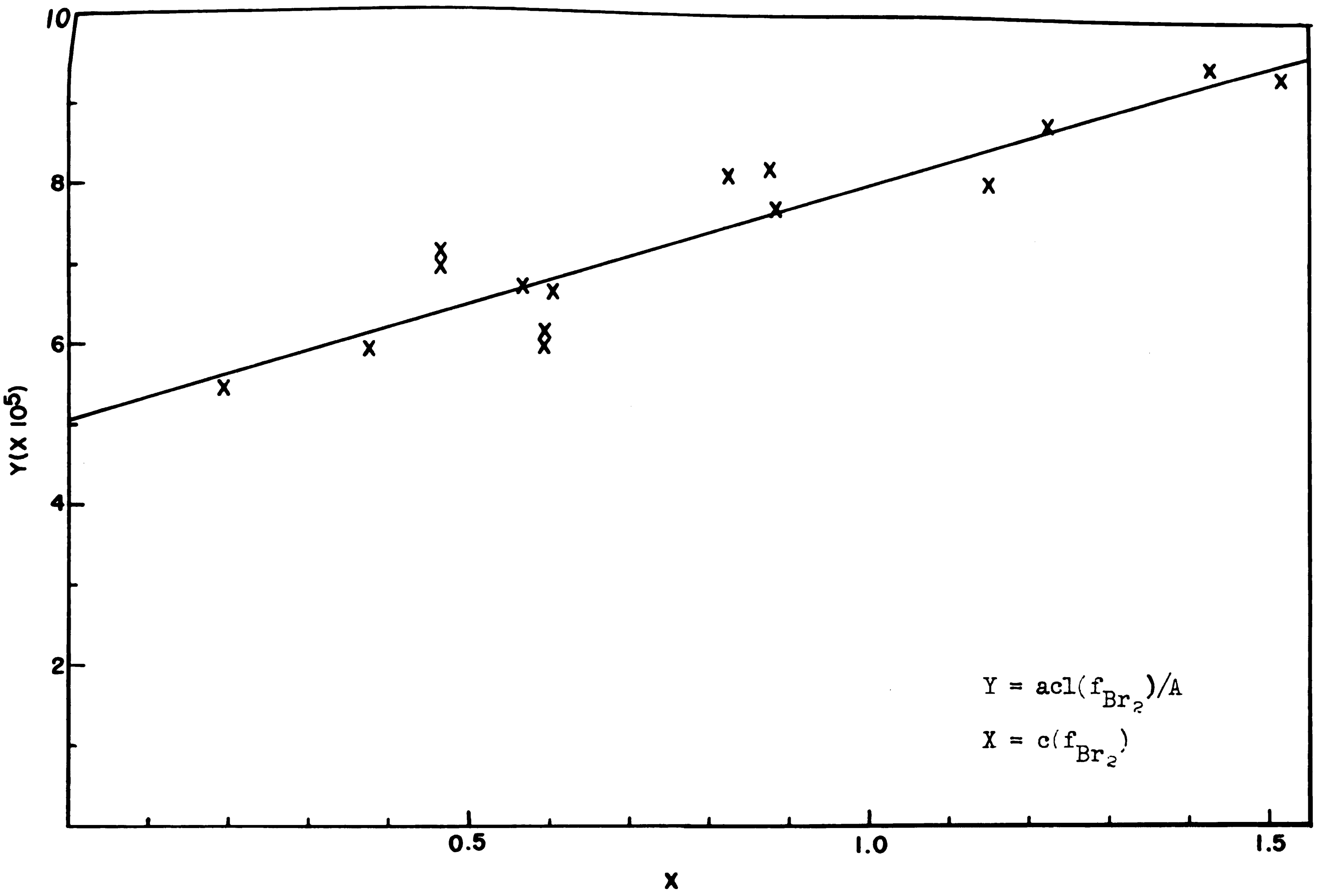


Figure 9. Test of the linear relationship used for determination of the formation equilibrium constant, K_4, and the molar extinction coefficient, e_{2380}, for dibromochloride ion. Hydrolysis neglected. (Values plotted are listed in Table IV.)

TABLE IV

DETERMINATION OF THE FORMATION EQUILIBRIUM CONSTANT, K_4, AND THE MOLAR EXTINCTION COEFFICIENT, e_{2380}, FOR DIBROMOCHLORIDE ION. HYDROLYSIS NEGLECTED

(Data Used in Least Squares Treatment)

Run No.	Initial Br_2 Conc. (a) (moles/liter) (x 10^4)	Initial NaCl Conc. (c) (moles/liter)	Br_2 Activity (Coef. (f)*)	Absorbance (A) at 2660Å (1 mm. light path)	X = cf (x 10)	Y = aclf/A (x 10^5)	XY (x 10^5)	X^2 (x 10)
155	3.91	0.7267	1.204	0.420	8.751	8.137	7.120	7.657
156	3.98	0.9571	1.279	0.567	12.24	8.651	10.59	14.98
157	4.02	0.5017	1.135	0.341	5.695	6.708	3.820	3.243
158	3.96	0.3449	1.090	0.251	3.760	5.929	2.229	1.414
159	3.73	0.1766	1.047	0.126	1.927	5.464	1.053	0.3712
160	4.09	0.7324	1.203	0.469	8.809	7.683	6.768	7.759
161	9.20	0.5274	1.144	0.835	6.031	6.645	4.008	3.638
162	8.75	0.4183	1.114	0.567	4.661	7.196	3.354	2.172
163	9.40	0.4193	1.115	0.630	4.673	6.969	3.257	2.184
164	8.80	0.6901	1.194	0.899	8.236	8.058	6.637	6.784
165	9.12	1.079	1.322	1.385	14.26	9.394	13.40	20.33
166	7.93	0.5215	1.139	0.790	5.941	5.963	3.543	3.529
167	9.54	0.5232	1.140	0.925	5.963	6.149	3.666	3.556
168	8.97	0.9102	1.263	1.335	11.50	7.905	9.089	13.22
169	9.43	1.134	1.336	1.545	15.16	9.248	14.02	22.97

* $f = f_{Br_2}$

$\sum X = 1.175 \times 10$

$\sum Y = 1.101 \times 10^{-3}$

$\sum XY = 9.254 \times 10^{-4}$

$\sum X^2 = 1.138 \times 10$

Results of Least Squares Analysis:

Intercept = 5.081×10^{-5}

Slope = 2.881×10^{-5}

$e_{2380} = 1/\text{slope} = 3.47 \times 10^4$

$K_4 = 1/(\text{intercept})(e_{2380}) = 5.67 \times 10^{-1}$ liter mole^{-1}

our discrepancy, and it was decided to attempt a hydrolysis correction in our calculations. The derivation of the expressions used in the calculations is as follows. Consider first the trihalide equilibrium,

$$Br_2 + Cl^- = Br_2Cl^-$$

The equilibrium constant is

$$K_4 = \frac{z}{(f_{Br_2})(a - x - z)c} \qquad (1)$$

Here, a is the initial bromine concentration, z is the equilibrium trihalide concentration, x is the extent of the hydrolysis reaction (as in Method 2 for the tribromide system), c is the initial concentration of chloride, and f_{Br_2} is the activity coefficient of bromine in the salt solution. The assumption has again been made that the activity coefficients of the trihalide and halide ions are essentially equal. The accompanying hydrolysis reaction is, as before,

$$H_2O + Br_2 = HOBr + Br^- + H^+$$

The equilibrium constant for this reaction is

$$K_h = \frac{x^3}{(a - x - z)} \cdot \frac{(f_{H^+})(f_{Br^-})(f_{HOBr})}{(f_{Br_2})}$$

$$= \frac{x^3}{(a - x - z)} (f_{\pm HBr})^2 \qquad (2)$$

It has again been assumed that the activity of the bromine is equal to that of the hypobromous acid; thus cancellation of these quantities gives equation (2). Substituting the expression, A/el, for z and solving (1) for x gives

$$x = a - A/el \left[\frac{K_4c(f_{Br_2}) + 1}{K_4c(f_{Br_2})} \right] \qquad (3)$$

Solving (2) for the expression, $(a - x - z)$, with subsequent substitution of this quantity into (1) gives, upon solution for z,

$$z = \frac{K_4cx^3}{K_h} (f_{\pm HBr})^2(f_{Br_2}) = A/el \qquad (4)$$

Substitution of (3) into (4) and rearranging gives

$$\left[\frac{AK_h l^2 e^2 (f_{Br_2})^2}{(f_{\pm HBr})^2} \right]^{\frac{1}{3}} (K_4e)^{\frac{2}{3}} = acl(f_{Br_2})(K_4e) - Ac(f_{Br_2})(K_4) - A \qquad (5)$$

For simplification, let (5) be represented as follows:

$$tX_1 = uX_2 - vX_3 - A \qquad (6)$$

Here, $X_1 = (K_4e)^{\frac{2}{3}}$, $X_2 = K_4e$, and $X_3 = K_4$. The significance of the quantities, t, u, and v, is apparent from a comparison of equations (5) and (6). Division of (6) by t gives

$$X_1 = (u/t)X_2 - (v/t)X_3 - A/t$$

or

$$X_1 = u'X_2 - v'X_3 - w' \qquad (7)$$

where $u' = u/t$, $v' = v/t$, and $w' = A/t$.

For any two individual runs, we would have:

Run #1 $X_1 = u_1'X_2 - v_1'X_3 - w_1'$

Run #2 $X_1 = u_2'X_2 - v_2'X_3 - w_2'$

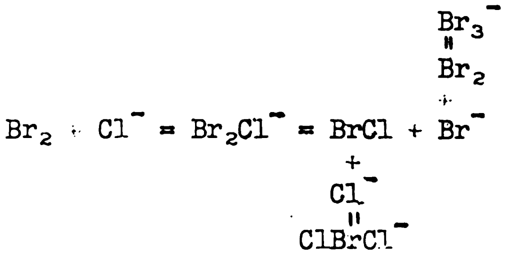
Eliminating X_1 from the last two equations and rearranging gives

$$\frac{(w_1' - w_2')}{(u_2' - u_1')} = \frac{(v_2' - v_1')}{(u_2' - u_1')} X_3 - X_2 \qquad (8)$$

Since X_2 and X_3 are both constants, then a plot of the quantity on the left side of equation (8) versus the coefficient of X_3 should give a straight line with slope and intercept equal to X_3 and $-X_2$ respectively. Ten of the runs applicable to this treatment were considered in the calculations. Table V shows the values of u', v', and w' as calculated from the data for each of the ten runs. Table VI gives the calculated values of the two quantities plotted for each of the pair of runs considered. Figure 10 shows the resulting plot.

Examination of the graph clearly reveals that the hydrolysis corrections alone do not alter the results markedly. An approximate calculation, directly from the graph, leads to approximate values of 0.75 liter and mole^{-1} and 3.3×10^{4} for K_4 and e_{2380}, respectively. A least squares analysis did not seem to be warranted because of the scatter of the results of these calculations.

It appears that some effects considerably more pronounced than hydrolysis are necessary to explain the discrepancy in the results. A possible reaction sequence is the following:



$$\begin{array}{ccccccccc} & & & & & & & & \mathrm{Br_3^-} \\ & & & & & & & & \| \\ & & & & & & & & \mathrm{Br_2} \\ & & & & & & & & + \\ \mathrm{Br_2} & + & \mathrm{Cl^-} & = & \mathrm{Br_2Cl^-} & = & \mathrm{BrCl} & + & \mathrm{Br^-} \\ & & & & & & + & & \\ & & & & & & \mathrm{Cl^-} & & \\ & & & & & & \| & & \\ & & & & & & \mathrm{ClBrCl^-} & & \end{array}$$

TABLE V

CALCULATED VALUES USED FOR DETERMINATION OF THE FORMATION EQUILIBRIUM CONSTANT, K_4, AND THE MOLAR EXTINCTION COEFFICIENT, e_{2380}, FOR DIBROMOCHLORIDE ION

HYDROLYSIS CONSIDERED

(Value of $K_h = 5.8 \times 10^{-9}$ used in Calculations)*

Run No.	u' (x 10)	v' (x 10^{-3})	w' (x 10^{-3})
156	1.144	1.630	1.332
157	1.015	0.8618	1.513
158	0.9657	0.6092	1.621
159	0.9170	0.3102	1.678
160	1.093	1.253	1.422
161	1.756	1.594	2.643
165	2.094	3.178	2.229
167	1.751	1.698	2.847
168	1.887	2.808	2.442
169	2.139	3.506	2.313

$$u' = \frac{acl(f_{Br_2})}{\left[\dfrac{AK_h l^2 c^2 (f_{Br_2})^2}{(f_{\pm HBr})^2}\right]^{\frac{1}{3}}} \qquad v' = \frac{Ac(f_{Br_2})}{\left[\dfrac{AK_h l^2 c^2 (f_{Br_2})^2}{(f_{\pm HBr})^2}\right]^{\frac{1}{3}}} \qquad w' = \frac{A}{\left[\dfrac{AK_h l^2 c^2 (f_{Br_2})^2}{(f_{\pm HBr})^2}\right]^{\frac{1}{3}}}$$

---

*Literature Value (4)

TABLE VI

CALCULATED VALUES USED FOR DETERMINATION OF THE FORMATION EQUILIBRIUM CONSTANT, K_4, AND THE MOLAR EXTINCTION COEFFICIENT, e_{2380}, FOR DIBROMOCHLORIDE ION

HYDROLYSIS CONSIDERED

Runs No.	$\frac{(w_1' - w_2')}{(u_2' - u_1')}$ (x 10^{-4})	$\frac{(v_2' - v_1')}{(u_2' - u_1')}$ (x 10^{-4})
156 and 161	-2.142	-0.05847
156 and 165	-0.9444	1.630
156 and 167	-2.498	0.1118
156 and 168	-1.494	1.585
156 and 169	-0.9860	1.885
157 and 161	-1.524	0.9881
157 and 165	-0.6632	2.147
157 and 167	-1.813	1.136
157 and 168	-1.019	2.232
157 and 169	-0.7114	2.352
158 and 161	-1.294	1.246
158 and 165	-0.5391	2.277
158 and 167	-1.563	1.387
158 and 168	-0.8916	2.387
158 and 169	-0.5901	2.467
159 and 161	-1.150	1.530
159 and 165	-0.4678	2.437
159 and 167	-1.402	1.664
159 and 168	-0.7873	2.575
159 and 169	-0.5194	2.615
160 and 161	-1.840	0.5145
160 and 165	-0.8057	1.923
160 and 167	-2.166	0.6763
160 and 168	-1.284	1.958
160 and 169	-0.8513	2.153

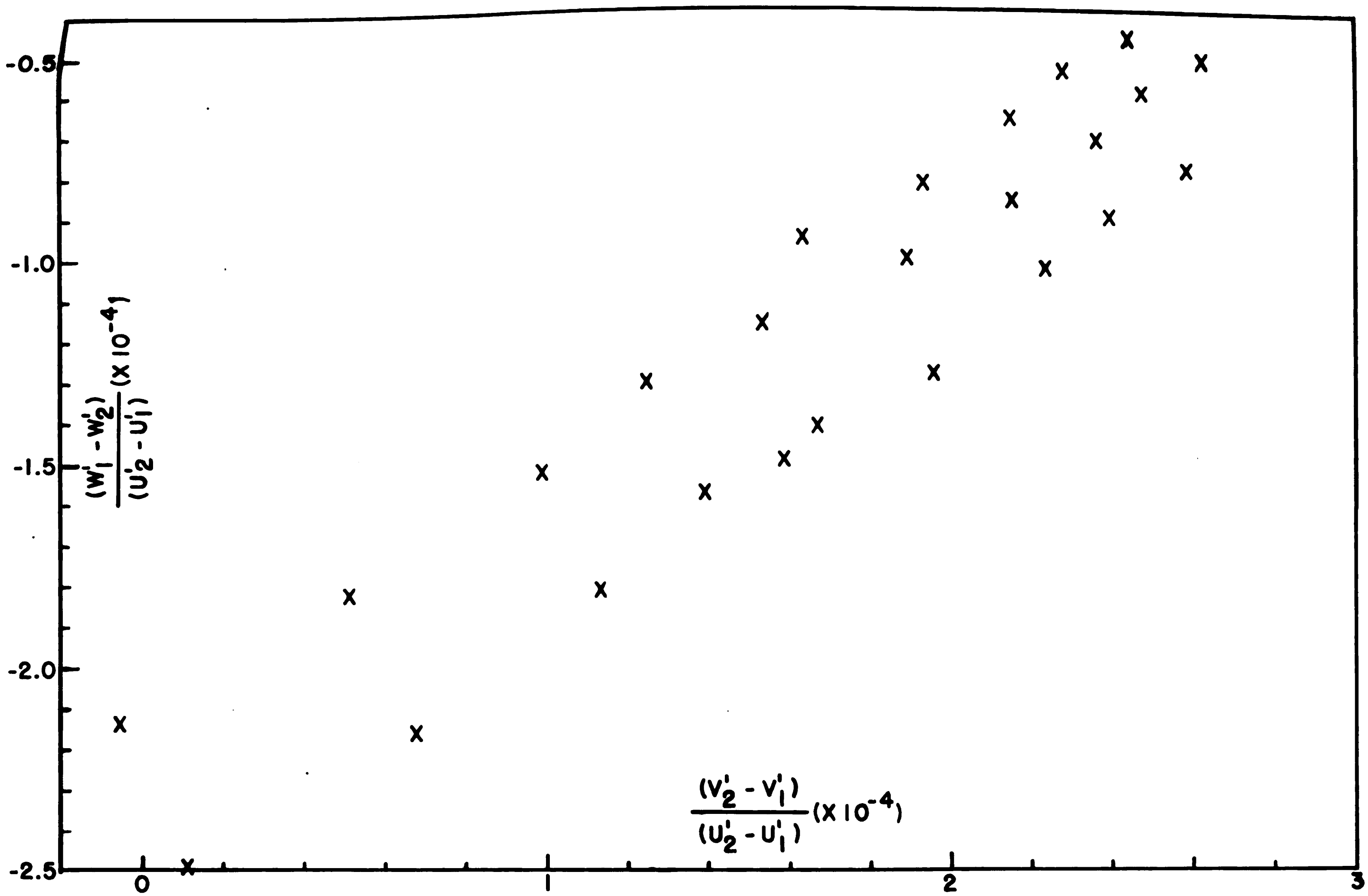


Figure 10. Test of the linear relationship used for determination of the formation equilibrium constant, K_4, and the molar extinction coefficient, e_{2380}, for dibromochloride ion. Hydrolysis considered. (Values plotted are listed in Table VI.)

The complete mathematical treatment of this sequence of reactions cannot be carried out with the available data. However, since these additional effects, as well as hydrolysis, would be retarded by added bromide, it was decided to modify the spectrophotometric approach to the dibromochloride equilibrium by study of the system, water-bromine-sodium chloride-sodium bromide.

The Water-Bromine-Sodium Chloride-Sodium Bromide System

Introduction

The study of this system was undertaken in an attempt to minimize the possible side equilibria which complicated the interpretation of the water-bromine-chloride study.

The mathematical treatment of this system must consider the simultaneous equilibria,

$$Br_2 + Cl^- = Br_2Cl^-$$

and

$$Br_2 + Br^- = Br_3^-$$

The interpretation is somewhat complicated by the fact that the ultraviolet absorption bands of the two trihalide ions overlap slightly so that the tribromide ion concentration cannot be determined from its absorbance at 2660Å alone. In addition, the tribromide extinction coefficient must be known at whatever other wavelengths are used for estimating the concentration of the dibromochloride ion.

It was therefore necessary to determine values of the tribromide ion extinction coefficient at wavelengths other than its absorption maximum, 2660Å. The two wavelengths chosen were 2500 and 2380Å. The latter was chosen because the apparent maximum of the dibromochloride ion appeared to be located at this wavelength. The 2500Å value was decided upon because it represents a wavelength intermediate between the maxima for the two separate ions.

Determination of e_{2380} and e_{2500} for Tribromide Ion

The new extinction values required for the tribromide ion were readily obtained from scans of the tribromide band from the earlier study on that ion. The relationships used were simply

$$e_{2500} = e_{2660}(A_{2500}/A_{2660})$$

and

$$e_{2380} = e_{2660}(A_{2380}/A_{2660})$$

Not all of the runs made in the tribromide study could be used for the present calculations. In some cases, due to the fact that these present evaluations were not anticipated at the time, insufficient data were available--that is, absorbance readings for the required wavelengths were not recorded in all instances. However, a sufficient number of runs were studied over the necessary wavelength span to permit the desired calculations. For example, the evaluation of e_{2500} was made from the data obtained in seven of the fourteen runs studied. Similarly, five runs were involved for the evaluation of e_{2380}. The results of these calculations are shown in Table VII. It is apparent that the agreement of the extinction values is rather good, a fact which probably strengthens any interpretation of these first studies. Subsequent calculations for the mixed salt system, water-bromine-sodium bromide-sodium chloride, yield results which seem to add further validity to this belief.

TABLE VII

DATA USED FOR DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENTS, e_{2500} AND e_{2380}, FOR TRIBROMIDE ION

Run Number	Absorbance (A) at 2500Å (1 mm. light path)	Absorbance (A) at 2660Å (1 mm. light path)	Molar Ext. Coef. (e_{2500}) (liter/mole/cm.) (x 10^{-4})
138	0.071	0.145	1.69
139	0.150	0.265	1.63
140	0.370	0.748	1.71
144	0.365	0.752	1.68
145	0.504	1.03	1.69
147	0.619	1.28	1.67
148	0.580	1.21	1.66
		Mean =	1.68

Run Number	Absorbance (A) at 2380Å (1 mm. light path)	Absorbance (A) at 2660Å (1 mm. light path)	Molar Ext. Coef. (e_{2380}) (liter/mole/cm.) (x 10^{-3})
144	0.101	0.752	4.65
145	0.135	1.03	4.54
146	0.170	1.22	4.82
147	0.175	1.28	4.73
148	0.170	1.21	4.86
		Mean =	4.72

Determination of the Ratios, e_{2380}/e_{2660} and e_{2500}/e_{2660} for Dibromochloride Ion

The mixed salt system requires a different mathematical treatment from those used in the previous calculations. The development of one of the methods will now be shown.

Consider two wavelengths at which the molar extinction coefficients of the tribromide ion are known. Then,

$$A'_{T1} = e_{y1}(y) + e_{z1}(z) \qquad (1)$$

and

$$A'_{T2} = e_{y2}(y) + e_{z2}(z) \qquad (2)$$

The absorbances per unit length of cell at the two wavelengths, λ_1 and λ_2, are represented by A'_{T1} and A'_{T2}, respectively. (In the previous sections, the absorbance has been represented by A, i.e., the absorbance associated with the actual light path (1 mm.) of the cell used in the studies. However, in several of the subsequent derivations, it will be convenient to use the absorbance per unit length of cell; therefore, both notations, A and A', will be utilized). The concentration of the tribromide ion is denoted by y and that of the dibromochloride ion by z, the designation being the same as in the preceding sections. Molar extinction coefficients are again represented by e; e_{y1} would thus be that of the tribromide ion at the first wavelength, etc. The unknown extinction coefficients of the dibromochloride ion are e_{z1} and e_{z2}. By simultaneous solution of (1) and (2), y and z can be expressed in terms of absorbances and extinction coefficients, i.e.,

$$z = \frac{e_{y2}(A'_{T1}) - e_{y1}(A'_{T2})}{e_{y2}(e_{z1}) - e_{y1}(e_{z2})} \qquad (3)$$

and

$$y = \frac{e_{z2}(A'_{T1}) - e_{z1}(A'_{T2})}{e_{y1}(e_{z2}) - e_{y2}(e_{z1})} \qquad (4)$$

The two equilibria considered are

$$Br_2 + Br^- = Br_3^- \qquad (5)$$

and

$$Br_2 + Cl^- = Br_2Cl^- \qquad (6)$$

Using the definitions indicated for y and z, the equilibrium constants of (5) and (6) can be expressed as follows:

$$K_3 = \frac{y}{(f_{Br_2})(a - y - z)b} \qquad (7)$$

and

$$K_4 = \frac{z}{(f_{Br_2})(a - y - z)c} \qquad (8)$$

where a is the initial concentration of bromine, and b and c are the bromide and chloride concentrations respectively. Because of the relatively high values of b and c relative to a, the exact expressions, (b-y) and (c-z), representing the equilibrium concentrations of the two halide ions, have been simplified to b and c. As in the preceding studies, the activity coefficient of bromine is designated by f_{Br_2}, and activity coefficients of the ions can be considered to cancel from the expressions.

From (7) and (8),

$$\frac{K_3}{K_4} = \frac{cy}{bz} \qquad (9)$$

Substitution of the expressions for y and z, as given in (3) and (4), into (9) gives

$$\frac{K_3}{K_4} = \frac{[e_{zI}(A'_{T1}) - e_{z1}(A'_{T2})]c}{[e_{y1}(A'_{T2}) - e_{y2}(A'_{T1})]b} \qquad (10)$$

Rearrangement then results in the following:

$$\frac{[e_{y1}(A'_{T2}) - e_{y2}(A'_{T1})]K_3b}{e(A'_{T1})} = K_4(e_{z2}) - K_4(e_{z1})(A'_{T2}/A'_{T1}) \qquad (11)$$

The left hand side of the equation involves only known quantities. If the quantity on the left side of the equation is now plotted versus the quantity, A'_{T2}/A'_{T1}, a linear relationship should result. The slope of this plot should be equal to $-K_4(e_{z1})$ and the intercept equal to $K_4(e_{z2})$.

It is apparent that although none of the unknowns, K_4, e_{z1}, or e_{z2}, can be evaluated individually by this method, nevertheless, certain useful relationships can be determined. The determination of the slope and intercept values, as indicated above, permits evaluation of the quotient, e_{z1}/e_{z2}. Thus,

$$\frac{\text{slope}}{-(\text{intercept})} = \frac{-K_4(e_{z1})}{-K_4(e_{z2})} = \frac{e_{z1}}{e_{z2}} \qquad (12)$$

In all, three wavelengths, 2380, 2500, and 2660Å, were considered in the two series of calculations made. (It will be understood that whenever any pair of wavelengths is being considered, the subscript, 1, will refer to the shorter of the two wavelengths). Table VIII and Figure 11 (graph) show the results of application of this method to the two wavelengths, 2380 and 2660Å. The excellent linearity obtained affords verification of the method. The table also includes evaluation of the slope and intercept by a least squares analysis. For these two wavelengths, the ratio, e_{z1}/e_{z2}, was found to be 2.30. Table IX and Figure 12 show the results for the pair of wavelengths, 2500 and 2660Å. In this case, the ratio, e_{z1}/e_{z2}, was found to be 2.25. The values of K_3 and the extinction coefficients of the tribromide ion for the three wavelengths, determined from the tribromide study, were used in these calculations. These values are as follows: K_3 = 17.3 liter mole^{-1}, $e_{y-2380} = 4.72 \times 10^3$, $e_{y-2500} = 1.68 \times 10^4$, and $e_{y-2660} = 3.46 \times 10^4$. The pertinent experimental data used in the calculations are shown in Table X.

Determination of e_{2300}, e_{2500}, and e_{2660} for Dibromochloride Ion

In order to evaluate K_4, it is clear that some means independent of the above method must be found for the determination of the individual extinction coefficients of the dibromochloride ion. The two methods could then be used jointly to calculate K_4. One such method can be obtained from relationships which will now be derived. Solution of (7) for z gives, upon rearrangement,

TABLE VIII

CALCULATED VALUES USED FOR DETERMINATION OF THE RATIO OF THE MOLAR EXTINCTION COEFFICIENTS, e_{2380}/e_{2660}, FOR DIBROMOCHLORIDE ION

(Data Used in Least Squares Treatment)

Run No.	X	$Y \times 10^{-4}$	X^2	$XY \times 10^{-5}$
171	3.164	-7.759	10.01	-2.455
172	2.063	-4.539	4.255	-0.9376
173	1.477	-2.999	2.182	-0.4430
174	0.6367	-0.5482	0.4054	-0.03491
175	0.5433	-0.3026	0.2952	-0.01644
176	0.4749	-0.1548	0.2255	-0.007353
	ΣX = 8.359	ΣY = -16.303	ΣX^2 = 17.39	ΣXY = -3.894

$$X = \frac{A'_{T1}}{A'_{T2}}$$

$$Y = \frac{[e_{y1}(A'_{T2}) - e_{y2}(A'_{T1})]K_3 b}{c(A'_{T1})}$$

Results of Least Squares Analysis:

Intercept = 1.231×10^4

Slope = -2.834×10^4

$$\frac{e_{z1}}{e_{z2}} = \frac{e_{2380}}{e_{2660}} = \frac{\text{slope}}{-(\text{intercept})} = 2.30$$

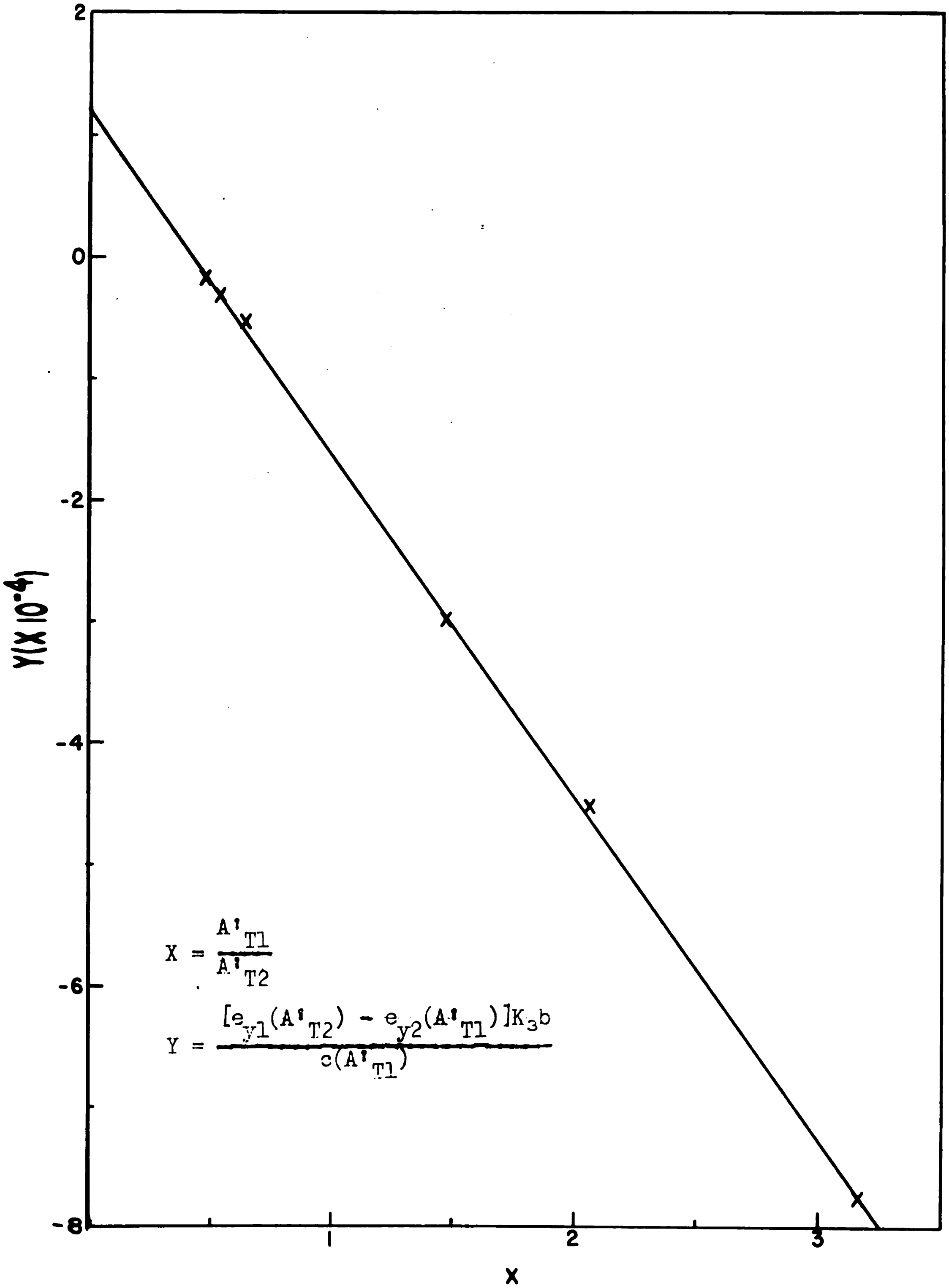


Figure 11. Test of the linear relationship used for determination of the ratio of the molar extinction coefficients, e_{2380}/e_{2660}, for dibromochloride ion. (Values plotted are listed in Table VIII.)

TABLE IX

CALCULATED VALUES USED FOR DETERMINATION OF THE RATIO OF THE MOLAR EXTINCTION COEFFICIENTS, e_{2500}/e_{2660}, FOR DIBROMOCHLORIDE ION

(Data Used in Least Squares Treatment)

Run No.	X	$Y \times 10^{-4}$	X^2	$XY \times 10^{-4}$
171	1.605	-3.028	2.576	-4.860
172	1.308	-2.312	1.710	-3.023
173	1.089	-1.773	1.186	-1.931
174	0.6106	-0.4233	0.3728	-0.2584
175	0.5498	-0.2397	0.3022	-0.1318
176	0.4938	-0.1252	0.2439	-0.06218
	$\Sigma X = 5.656$	$\Sigma Y = -7.902$	$\Sigma X^2 = 6.391$	$\Sigma XY = -10.266$

$$X = \frac{A'_{T1}}{A'_{T2}}$$

$$Y = \frac{[e_{y1}(A'_{T2}) - e_{y2}(A'_{T1})]K_3 b}{c(A'_{T1})}$$

Results of Least Squares Analysis:

Intercept = 1.175×10^4

Slope = -2.644×10^4

$$\frac{e_{z1}}{2_{z2}} = \frac{e_{2500}}{e_{2660}} = \frac{\text{slope}}{-(\text{intercept})} = 2.25$$

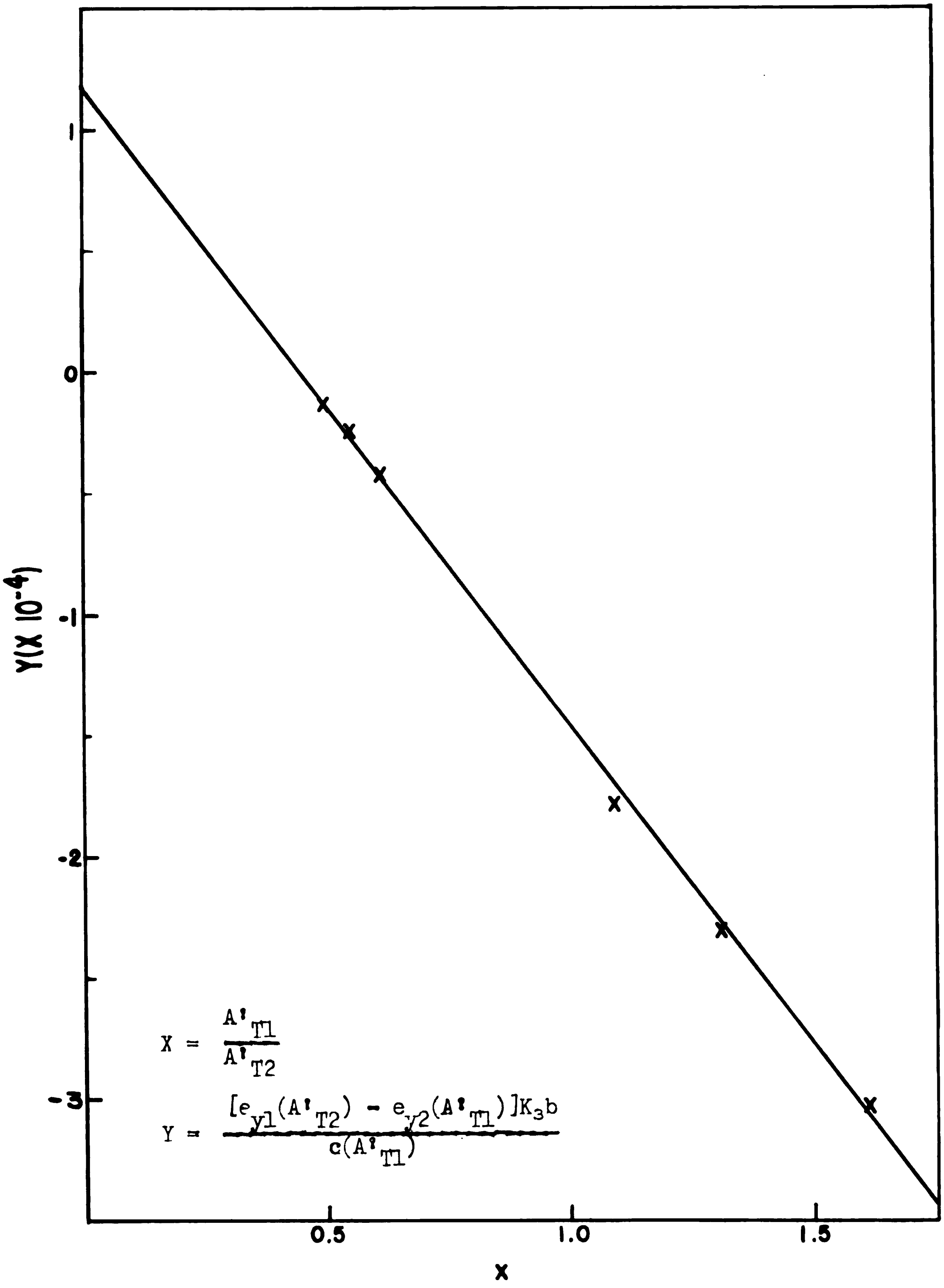


Figure 12. Test of the linear relationship used for determination of the ratio of the molar extinction coefficients, e_{2500}/e_{2660}, for dibromochloride ion. (Values plotted are listed in Table IX.)

TABLE X

PERTINENT DATA FOR SYSTEM: H_2O-Br_2-NaCl-NaBr

Run Number	Initial Br_2 Conc.(a) (moles/liter) (x 10^4)	Initial NaBr Conc.(b) (moles/liter) (x 10^2)	Initial NaCl Conc.(c) (moles/liter) (x 10)	Br_2 Activity Coef.(f)	Absorbances (A) (1 mm. light path)		
					2380Å	2500Å	2650Å
171	2.00	10.98	4.183	1.158	0.140	0.276	0.443
172	4.15	5.126	4.860	1.144	0.303	0.478	0.625
173	4.08	6.070	9.678	1.283	0.415	0.563	0.613
174	4.03	1.081	10.78	1.324	0.490	0.511	0.312
175	3.97	0.5004	9.168	1.268	0.427	0.422	0.232
176	9.37	0.2747	9.935	1.292	1.095	1.053	0.520

$$z = -\left[\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right] y + a \qquad (7a)$$

Substitution of this expression for z into (1) and (2), with rearrangement, gives,

$$\text{from (1)} \qquad A'_{T1} = \left[e_{y1} - e_{z1}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)\right] y + ae_{z1} \qquad (13)$$

$$\text{from (2)} \qquad A'_{T2} = \left[e_{y2} - e_{z2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)\right] y + ae_{z2} \qquad (14)$$

Equation (13) can also be expressed as follows:

$$\frac{A'_{T1} - ae_{z1}}{\left[e_{y1} - e_{z1}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)\right] y} = 1 \qquad (13a)$$

Similarly, (14) may be represented in the form,

$$\frac{A'_{T2} - ae_{z2}}{\left[e_{y2} - e_{z2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)\right] y} = 1 \qquad (14a)$$

Equating (13a) and (14a), with subsequent rearrangement, then gives

$$\left[\frac{A'_{T1}(e_{y2}) - A'_{T2}(e_{y1})}{ae_{y2} - A'_{T2} \quad \left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)}\right] =$$

$$e_{z1} = e_{z2} \left[\frac{A'_{T1} \left(\frac{1 + (f_{Br_2})K_3 b}{(f_{Br_2})K_3 b} \right) - ae_{y1}}{ae_{y2} - A'_{T2} \left(\frac{(1 + (f_{Br_2})K_3 b}{(f_{Br_2})K_3 b} \right)} \right] \qquad (15)$$

For any individual run, the terms within the brackets are all known quantities. Therefore, a plot of the value of the left side of the equation versus the bracketed quantity on the right side should result in a straight line. The slope and intercept of the plot would then be e_{z2} and e_{z1} respectively. Calculations were made in this manner.

Table XI shows the results as obtained by (15) for the two wavelengths 2380 and 2660Å. Figure 13 shows the plot for these values. Table XII and Figure 14 show the analogous results for the 2500-2660Å pair. The important results from these calculations are the individual extinction coefficients for the three wavelengths considered. The values calculated are as follows:

$e_{z-2380} = 2.07 \times 10^4$

$e_{z-2500} = 1.98 \times 10^4$

$e_{z-2660} = 8.36 \times 10^3$ and 8.42×10^3 (Mean = 8.39×10^3)

The two values for the 2660Å wavelength resulted from the fact that this wavelength was considered in both sets of calculations. The pertinent data used in the preceding calculations are shown in Table X.

Determination of K_4

Returning to the first method (for the 2380-2660Å pair), the slope was found to be -2.834×10^4 and the intercept equal to 1.231×10^4

TABLE XI

CALCULATED VALUES USED FOR DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENTS, e_{2380} AND e_{2660}, FOR DIBROMOCHLORIDE ION

(Data Used in Least Squares Treatment)

Run No.	X	$Y \times 10^{-4}$	$XY \times 10^{-4}$	$X^2 \times 10^{-1}$
172	2.080	3.864	8.039	0.4327
173	1.543	3.337	5.150	0.2382
174	-12.73	-8.645	110.0	16.20
175	-4.227	-1.400	5.919	1.786
176	-3.188	-0.6007	1.915	1.016
	$\Sigma X = -16.52$	$\Sigma Y = -3.445$	$\Sigma XY = 131.0$	$\Sigma X^2 = 19.68$

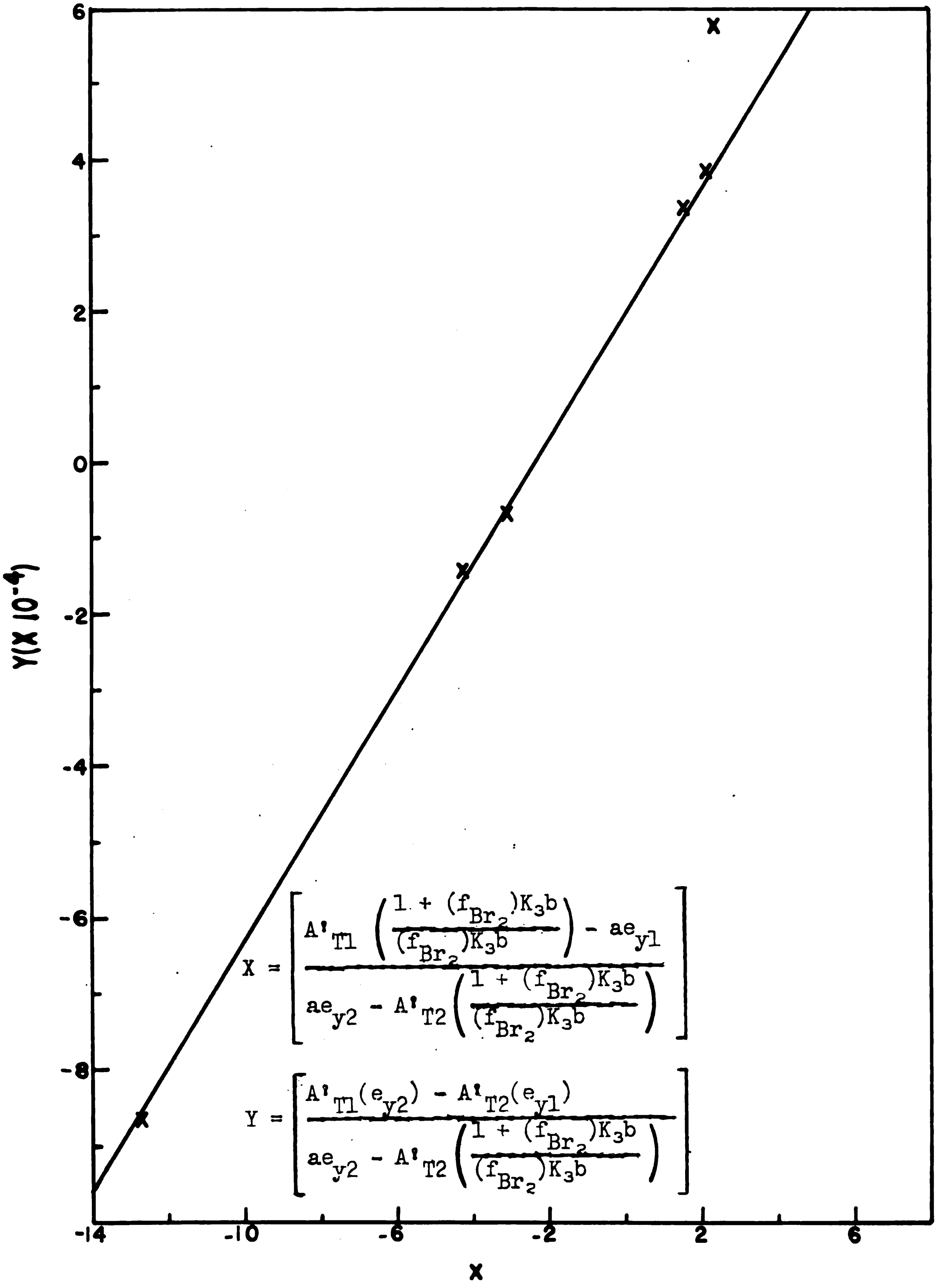
$$X = \left[\frac{A'_{T1} \left(\frac{1 + (f_{Br_2})K_3 b}{(f_{Br_2})K_3 b} \right) - ae_{y1}}{ae_{y2} - A'_{T2} \left(\frac{1 + (f_{Br_2})K_3 b}{(f_{Br_2})K_3 b} \right)} \right]$$

$$Y = \left[\frac{A'_{T1}(e_{y2}) - A'_{T2}(e_{y1})}{ae_{y2} - A'_{T2} \left(\frac{1 + (f_{Br_2})K_3 b}{(f_{Br_2})K_3 b} \right)} \right]$$

Results of Least Squares Analysis:

$e_{z1} = e_{z-2380}$ = intercept - 2.07×10^4

$e_{z2} = e_{z-2660}$ = slope = 8.36×10^3



$$X = \left[\frac{A'_{T1}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right) - ae_{y1}}{ae_{y2} - A'_{T2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)} \right]$$

$$Y = \left[\frac{A'_{T1}(e_{y2}) - A'_{T2}(e_{y1})}{ae_{y2} - A'_{T2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)} \right]$$

Figure 13. Test of the linear relationship used for determination of the molar extinction coefficients, e_{2380} and e_{2660}, for dibromochloride ion. (Values plotted are listed in Table IX.)

TABLE XII

CALCULATED VALUES USED FOR DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENTS, e_{2500} AND e_{2660}, FOR DIBROMOCHLORIDE ION
(Data Used in Least Squares Treatment)

Run No.	X	$Y \times 10^{-4}$	$XY \times 10^{-4}$	$X^2 \times 10^{-1}$
172	1.296	3.105	4.023	0.1679
173	0.8624	2.676	2.308	0.07438
174	-10.61	-6.950	73.73	11.25
175	-3.684	-1.096	4.040	1.358
176	-2.871	-0.4698	1.349	0.8244
	$\Sigma X = -15.00$	$\Sigma Y = -2.735$	$\Sigma XY = 85.45$	$\Sigma X^2 = 13.67$

$$X = \left[\frac{A'_{T1}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right) - ae_{y1}}{ae_{y2} - A'_{T2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)} \right]$$

$$Y = \left[\frac{A'_{T1}(e_{y2}) - A'_{T2}(e_{y1})}{ae_{y2} - A'_{T2}\left(\frac{1 + (f_{Br_2})K_3b}{(f_{Br_2})K_3b}\right)} \right]$$

Results of Least Squares Analysis:

$e_{z1} = e_{z-2500} = \text{intercept} = 1.98 \times 10^4$

$e_{z2} = e_{z-2660} = \text{slope} = 8.42 \times 10^3$

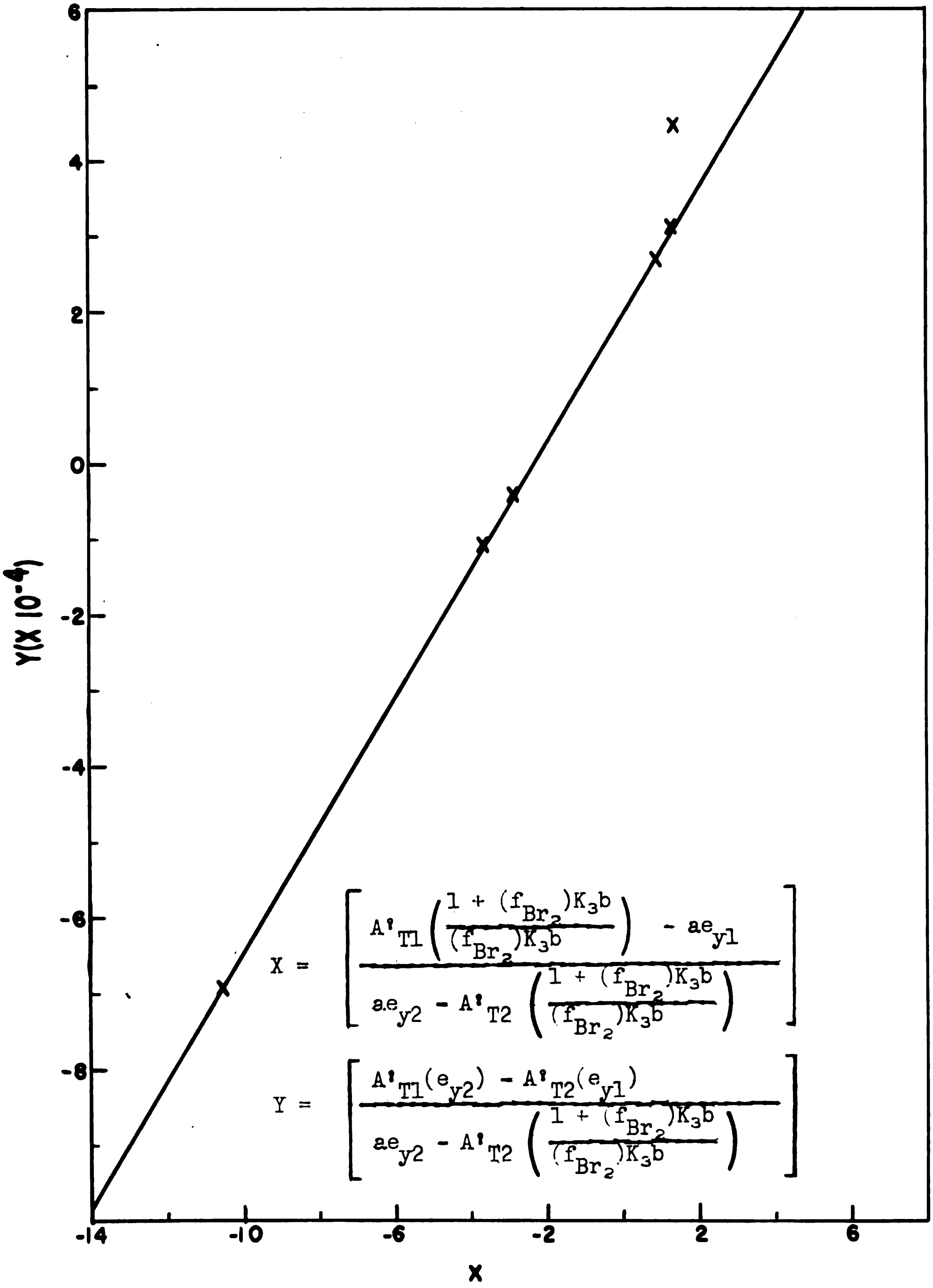


Figure 14. Test of the linear relationship used for determination of the molar extinction coefficients, e_{2500} and e_{2660}, for dibromochloride ion. (Values plotted are listed in Table XII.)

(Table VIII). From equation (11),

$$\text{slope} = -K_4 e_{z-2380}$$

and

$$\text{intercept} = K_4 e_{z-2660}$$

Using the extinction values for the dibromochloride ion as calculated by the second method (preceding paragraph),

$$\text{slope} = -2.834 \times 10^4 = -K_4(2.07 \times 10^4)$$

$$K_4 = 1.37$$

Again,

$$\text{intercept} = 1.231 \times 10^4 = K_4(8.39 \times 10^3)$$

$$K_4 = 1.47$$

Analogous calculations for the 2500-2660A pair are as follows: The slope and intercept values are -2.644×10^4 and 1.175×10^4, respectively (Table IX). Again using the calculated extinction values for the dibromochloride ion and equation (11),

$$\text{slope} = -2.644 \times 10^4 = -K_4(1.98 \times 10^4)$$

$$K_4 = 1.33$$

and

$$\text{intercept} = 1.175 \times 10^4 = K_4(8.39 \times 10^3)$$

$$K_4 = 1.40$$

The mean value of K_4 obtained from these four calculated values is 1.39.

It will be recalled that the ratios of the extinction coefficients were also evaluated by the first method. Since the individual coefficients were determined by the second method, it is interesting to compare these results. For the 2380-2660Å pair, $(e_{z-2380})/(e_{z-2660}) = 2.30$ (Table VIII). With the 2500-2660Å pair, $(e_{z-2500})/e_{z-2660}) = 2.25$ (Table IX). Using the individual values from the second method,

$$(e_{z-2380})/(e_{z-2660}) = (2.07 \times 10^4)/(8.39 \times 10^3) = 2.47$$

and

$$(e_{z-2500})/(e_{z-2660}) = (1.98 \times 10^4)/(8.39 \times 10^3) = 2.36$$

It is seen that the preceding results are reasonably concordant. The mean value of 1.39 obtained for the formation equilibrium constant is in very good agreement with the results reported in the literature (from distribution studies). In addition, the check on the ratios of the extinction coefficient values is gratifying, particularly when one considers the two rather highly derived methods of approach.

Determination of Concentrations, Absorbances, and Extinction Coefficients of the Individual Trihalide Ions

The molar extinction coefficients calculated for the two trihalide ions at the three wavelengths, 2380, 2500, and 2660Å, permit further computation. It is now possible to claculate, for each run, the concentrations of the individual ions as well as the absorption contributed by each.

The tribromide ion concentration, y, can be determined by use of the equation (page 54).

$$y = \frac{e_{z2}(A'_{T1}) - e_{z1}(A'_{T2})}{e_{y1}(e_{z2}) - e_{y2}(e_{z1})}$$

The notation is the same as that used in the preceding sections; thus, A'_{T1} would be the total absorbance per unit cell length at the shorter of the two wavelengths under consideration; e_{z1} would be the molar extinction coefficient of the dibromochloride ion at the same wavelength; etc. Using the computed extinction values of the two ions which are associated with the wavelengths, 2380 and 2660Å, the tribromide ion concentration, y, was calculated for each of the runs. These results are shown in Table XIII.

The absorbance of the tribromide ion, A_y, at each of the three wavelengths was then easily determined from the relationship,

$$A_y = e_y yl$$

(Hereafter, only the notation, A, i.e., the absorbance associated with the actual cell length, will be used.) The preceding equation can be used for any wavelength at which the molar extinction coefficient is known. In the present case, the absorbance at each of the three wavelengths was calculated. These results are included in Table XIV. Since the total absorbance at each of the wavelengths is equal to the sum of the absorbances of the individual trihalide ions, the absorbance due to the dibromochloride ion, A_z, is given by

$$A_z = A_T - A_y$$

Calculations were made for the three wavelengths. These results are also included in Table XIV. With the absorbance values for the dibromochloride ion known, the concentration, z, can be evaluated

TABLE XIII

CONCENTRATIONS OF THE VARIOUS SPECIES PRESENT IN SYSTEM H_2O-Br_2-NaCl-NaBr

Run No.	Initial Br_2 Conc.(a) (moles/liter) (x 10^4)	Initial NaBr Conc.(b) (moles/liter) (x 10^2)	Initial NaCl Conc.(c) (moles/liter) (x 10)	Equil. Br_3^- Conc.(y) (moles/liter) (x 10^4)	Equil. Br_2Cl^- Conc.(z) (moles/liter) (x 10^4)			
					2380Å	2500Å	2660Å	Mean
171	2.00	10.98	4.183	1.18	0.406	0.389	0.405	0.400
172	4.15	5.126	4.860	1.54	1.11	1.11	1.11	1.11
173	4.08	6.070	9.678	1.36	1.70	1.69	1.69	1.69
174	4.03	1.081	10.78	0.347	2.29	2.29	2.29	2.29
175	3.97	0.5004	9.168	0.180	2.02	1.98	2.03	2.01
176	9.37	0.2747	9.935	0.233	5.24	5.12	5.23	5.20

TABLE XIV

CALCULATED ABSORBANCES OF TRIBROMIDE AND DIBROMOCHLORIDE IONS IN STUDIES OF SYSTEM: H_2O-Br_2-NaCl-NaBr

Wavelength (Å)	Total Absorbance(A_T) (1 mm. light path)	Br_3^- Absorbance(A_Y) (1 mm. light path)	Br_2Cl^- Absorbance(A_Z) (1 mm. light path)
Run 171			
2380	0.140	0.056	0.084
2500	0.276	0.199	0.077
2660	0.443	0.409	0.034
Run 172			
2380	0.303	0.073	0.230
2500	0.478	0.258	0.220
2660	0.625	0.532	0.093
Run 173			
2380	0.415	0.064	0.351
2400	0.445	0.082	0.363
2500	0.563	0.229	0.334
2600	0.628	0.423	0.205
2660	0.613	0.471	0.142
2700	0.562	0.465	0.097
2800	0.383	0.345	0.038
3000	0.138	0.136	0.002
Run 174			
2380	0.490	0.016	0.474
2500	0.511	0.058	0.453
2660	0.312	0.120	0.192
Run 175			
2380	0.427	0.009	0.418
2500	0.422	0.030	0.392
2660	0.232	0.062	0.170
Run 176			
2380	1.095	0.011	1.084
2500	1.053	0.039	1.014
2660	0.520	0.081	0.439

directly from the Beer Law expression in the form,

$$z = A_z/e_z l$$

The computations were made for the three wavelengths of concern; the results are given in Table XIII. These calculations reflect the internal consistency of the results, as shown by comparing the values of the dibromochloride ion concentration obtained independently from the extinction values of the three wavelengths.

It was most desirable to ascertain the form of the dibromochloride ion absorption band. With still further treatment of the available data, an appreciable portion of the band was characterized. The manner by which this information was obtained will now be discussed. Again, it was necessary to return to the tribromide ion study (system: water-bromine-sodium bromide). The data obtained for one of the runs (run 144) of this earlier study permitted evaluation of the molar extinction coefficients of the tribromide ion at wavelengths other than the three considered to this point. For a given run, absorbances and extinction values at any two wavelengths have the following relationship:

$$e_{y1} = (A_1/A_2)e_{y2}$$

Using the extinction coefficient of the tribromide ion at 2660Å (e = 3.46×10^4), the absorbance at 2660Å, and the absorbance at a second wavelength, the extinction coefficient at this second wavelength was evaluated. The procedure was repeated for obtaining the coefficient values at a number of wavelengths. The results are shown in Table XV.

TABLE XV

MOLAR EXTINCTION COEFFICIENTS OF THE TRIBROMIDE AND DIBROMOCHLORIDE IONS AT VARIOUS WAVELENGTHS

Wavelength (Å)	Tribromide Ion Ext. Coef. (e_y) (liter/mole/cm.) (x 10^{-4})	Dibromochloride Ion Ext. Coef.(e_z) (liter/mole/cm.) (x 10^{-4})
2380	0.472	2.07
2400	0.598	2.15
2500	1.68	1.98
2600	3.1	1.22
2660	3.46	0.839
2700	3.41	0.579
2800	2.53	0.231
3000	0.998	0.0118

Using the data from one of the mixed salt runs (run 173), together with the newly acquired extinction values for the tribromide ion, it was then possible to evaluate the extinction values for the dibromochloride ion at these additional wavelengths. The same approach used for computing the extinction coefficients at the first three wavelengths was again utilized. The absorbance of the tribromide ion was first calculated at each of the wavelengths by use of the equation,

$$A_y = e_y yl$$

Absorbances of the dibromochloride ion were then determined, again by the expression,

$$A_z = A_T - A_y$$

Finally, the extinction values for the dibromochloride ion were evaluated by the simple expression,

$$e_z = A_z/zl$$

The results of these calculations are shown in Table XIV (Absorbances) and Table XV (Extinction Coefficients).

Using the results of the preceding paragraphs, a graphical analysis was then made for run 173. Figure 15 shows three plotted curves. Curve A represents the absorption for the system as obtained directly from the experimental data; it is the composite absorption curve resulting from the absorption of both trihalide ions. The absorptions due to the tribromide and dibromochloride ions, each considered independently, are shown by curves B and C respectively. It is seen that the

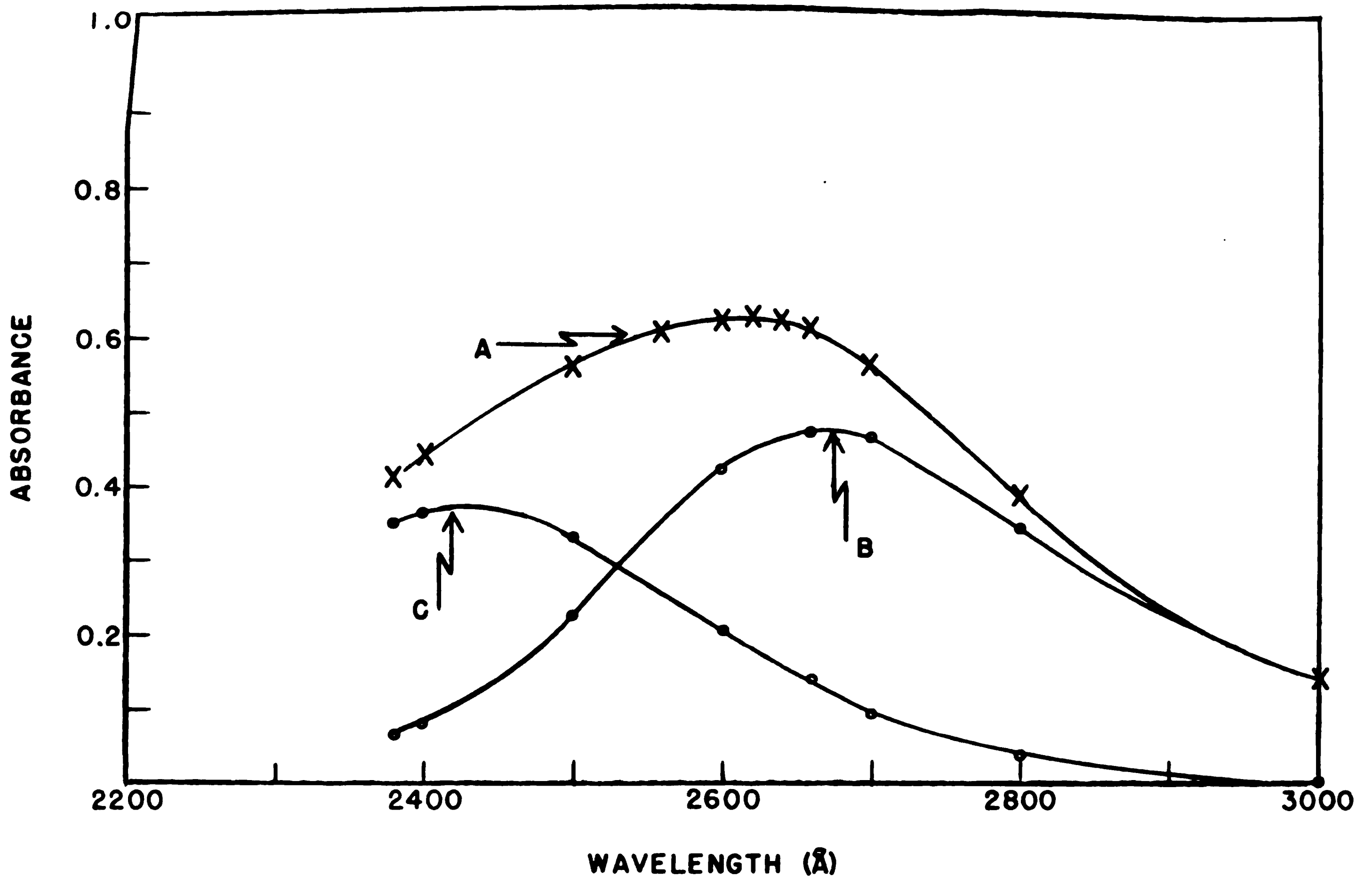


Figure 15. Analysis of ultraviolet absorption spectrum of the H_2O-Br_2-NaCl-NaBr system at 25°C. Spectrum A was obtained directly from the experimental data; spectra B and C represent the calculated absorptions of tribromide and dibromochloride ions, respectively. (Run 173)

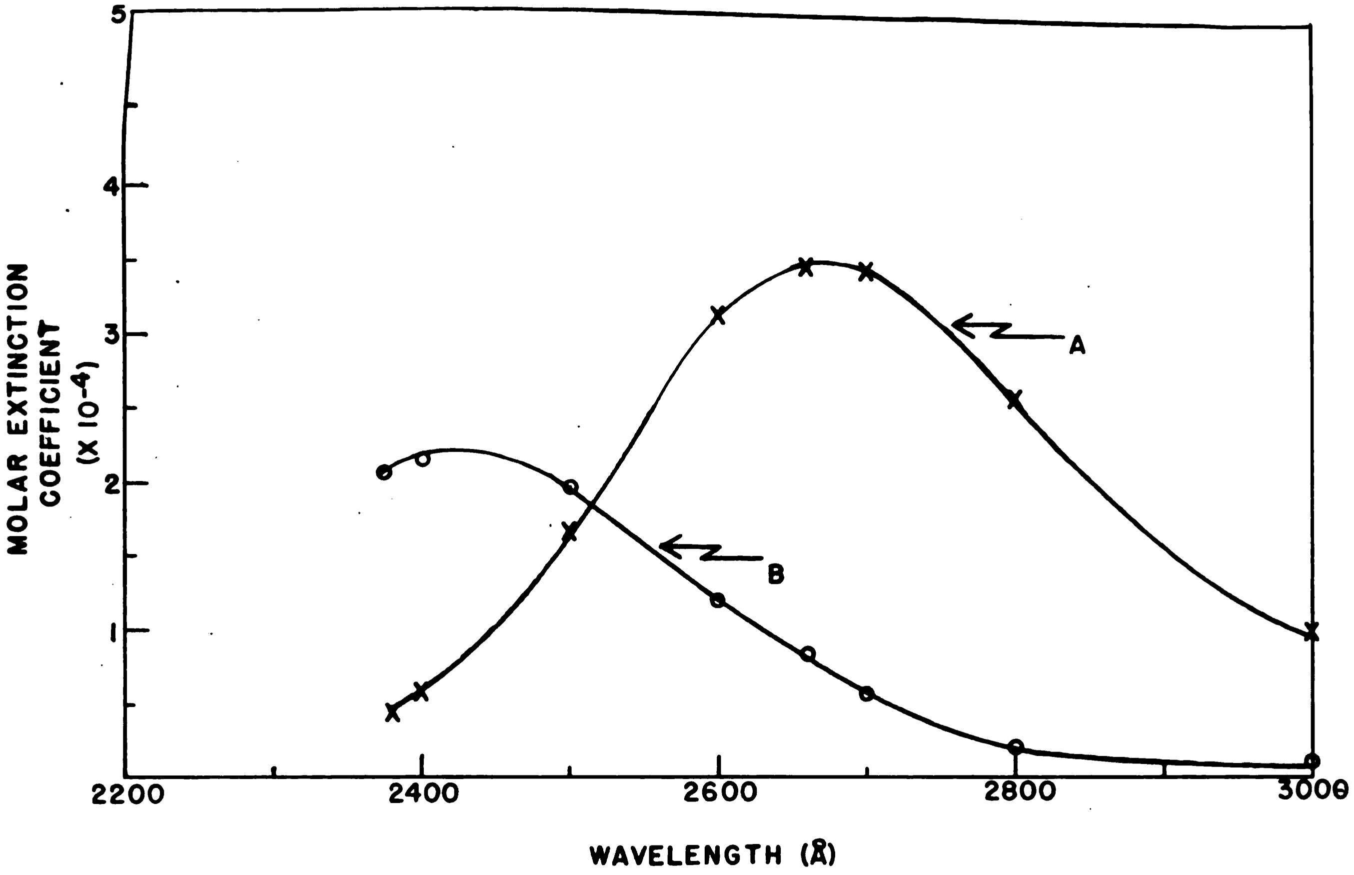


Figure 16. Molar extinction coefficient-wavelength relationship for tribromide and dibromochloride ions. Curve A - Tribromide ion. Curve B - Dibromochloride ion.

dibromochloride ion band has its absorption maximum at approximately 2430Å. Since the absorbance at this wavelength can be closely approximated from spectrum C, it was possible to calculate the extinction coefficient for the band peak. The computation is as follows:

$$e_{z-2430} = A_{z-2430}/zl = \frac{0.370}{1.69 \times 10^{-4}(0.1)} = 2.19 \times 10^{4}$$

It may be concluded that the results obtained strongly support the assignment of the indicated absorption band to the dibromochloride ion.

EXPERIMENTAL

Source and Purification of Reagents

Water

Purification of the water was effected by two distillations. The first of these was distillation of the original tap distilled water from a dilute alkaline permanganate solution through a three foot column packed with glass beads; the column contained approximately six theoretical plates. A middle fraction from this first distillation then underwent a second distillation through a column similar to the first one. In the latter case, however, the distillation was carried out in a nitrogen atmosphere. Again, only a middle fraction was collected. Purity of the product was determined conductimetrically. Conductance values were of the order of 0.5×10^{-6} reciprocal ohms in virtually every case.

Bromine

Bromine purification also utilized a distillation. The bromine was first refluxed over phosphorous pentoxide and potassium bromide for a period of one hour. This was followed by distillation with only a middle fraction retained. In a typical purification, approximately one hundred milliliters would be used initially; about fifty milliliters would be retained after the distillation. Mallinckrodt (N. F. V) bromine was the starting material. The phosphorous pentoxide and potassium bromide were both 'Baker Analyzed' Reagent products.

The purified bromine was subsequently stored in vacuo; the container was kept immersed in a dry ice-chloroform-carbon tetrachloride cooling bath. This purification is a slight modification of that used by Bauer and Daniels (31), who used barium oxide rather than phosphorous pentoxide.

Salts

Mallinckrodt "Analytical Reagent" Grade sodium bromide and chloride were used without further purification.

Apparatus

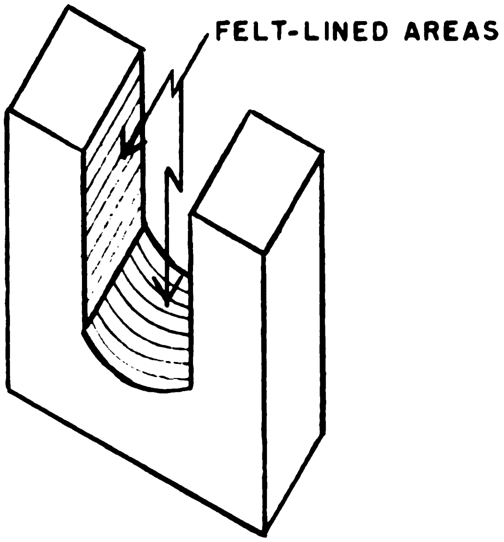
Spectrophotometers, Absorption Cells and Cell Holder

The early qualitative studies concerned with the water-bromine system were made with a Beckman DK-2 recording spectrophotometer. A pair of one centimeter quartz cells were used in this phase of the work.

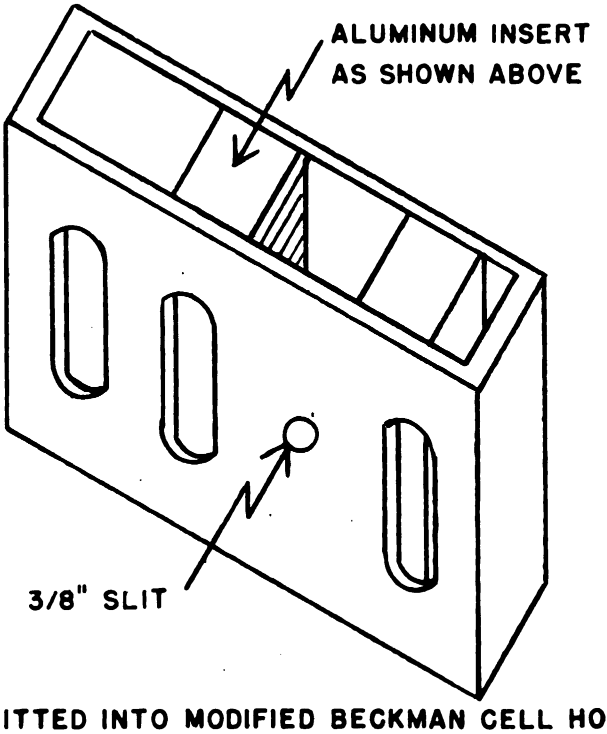
With the exception of these first studies, the remainder were made with a Beckman Model DU spectrophotometer. A one millimeter cylindrical quartz cell was used for these quantitative runs.

All of the runs made with the Beckman DU were carried out at 25°C. The cell compartment was equipped with a pair of Beckman thermospacers, through which water from a thermostated bath was pumped. Temperatures were controlled, by these means, to approximately 25 ± 0.5°C.

The cylindrical shape of the special one millimeter cell required a special cell holder, since its diameter was too large for insertion into one of the rectangular compartments of the standard Beckman cell holder. A satisfactory holder was constructed by modification of one of the ordinary Beckman one-centimeter cell holders. A sketch of the modified piece is shown in Figure 17. The inner sections of the original holder were removed, and a U-shaped aluminum assembly was fitted into the resulting rectangular skeleton. In use, the cylindrical cell would be placed into the U-cavity, which was lined with felt to hold the cell in a secure position. The aluminum assembly was so positioned that the cell was centered with respect to the second of the four original cell positions in the holder. To eliminate light scattering and reflection, the diameter of the light beam was restricted to a 3/8 inch opening, which permitted light to pass through the cell without striking the side walls. With this arrangement, a reference cell could not be used. However, because of the more critical necessity for reproducing cell position with the small cylindrical cells, it was felt that the usual lateral motion of the entire cell holder to interchange sample and reference cells would not have been satisfactory. A somewhat less convenient but more reproducible technique was used, employing the one cell and making the necessary corrections. It was found that with the cell holder in a stationary position, the position of the cell was quite reproducible; for any one of the solutions studied, alternate removal and replacement of the cell invariably gave the same absorbance reading. Therefore, for any solution, the correction necessary was subtraction of the absorbance reading of the cell filled with the solvent, water. Since neither of the salts, sodium bromide or chloride, show any absorption in the range of wavelengths studied, this procedure proved to be a satisfactory one. In practice, while taking



ALUMINUM INSERT FOR SUPPORT OF 1 MM. QUARTZ CELL



INSERT FITTED INTO MODIFIED BECKMAN CELL HOLDER

Figure 17. Modified Cell Holder for the one millimeter quartz cell.

readings from wavelength to wavelength, the cell was first removed, and the instrument then balanced with no obstruction whatsoever in the optical path. This served as the reference balance, analogous, of course, to the usual balancing of the instrument with reference cell and solvent. In the calibration of the cell with solvent, the same reference was used; thus, the overall correction would simply be the absorption due to the cell and solvent. Since the latter are constant for any given wavelength, they would therefore represent the correction necessary in all of the runs. These corrections are listed below (Table XVI) for the wavelengths under consideration.

TABLE XVI

ABSORBANCE CORRECTIONS FOR THE ONE MILLIMETER QUARTZ CELL AND SOLVENT (WATER) AT VARIOUS WAVELENGTHS

Wavelength (Å)	Absorbance Correction
2380	-0.085
2400	-0.082
2500	-0.077
2600	-0.062
2660	-0.050
2700	-0.050
2800	-0.050
2900	-0.050
3000	-0.050

The indicated 1.000-millimeter optical-path length of the cell was checked by measuring the absorption of a reference solution. An alkaline solution of potassium chromate for this purpose has been described by Haupt (32). Included in Haupt's paper is a table of absorbance readings for the entire ultraviolet portion of the spectrum. The standard solution used was one containing 0.0400 g. of potassium chromate per liter in 0.05N potassium hydroxide. The results obtained in the present work as well as those reported by Haupt are shown in Table XVII.

TABLE XVII

RESULTS OF CHECK ON OPTICAL PATH LENGTH OF THE ONE MILLIMETER QUARTZ CELL BY USE OF A REFERENCE SOLUTION*

Wavelength(Å)	Absorbance Correction	Absorbance (Total)	Absorbance (Corrected)	Absorbance (from Haupt) (1 cm. light path)
2200	-0.078	0.118	0.040	0.446
2250	-0.073	0.093	0.020	0.221
2300	-0.074	0.090	0.016	0.171
2350	-0.078	0.098	0.020	0.210
2400	-0.082	0.098	0.029	0.295
2450	-0.080	0.119	0.039	0.396

*Haupt's studies with the reference solution are discussed above.

As indicated in the preceding discussion, the correction values represent the absorbance of the cell plus solvent versus air; the total absorbance is that of the solution plus cell versus air. The corrected values obtained are within experimental error smaller than Haupt's by the anticipated factor of ten.

The results of another interesting check are summarized below (Table XVIII). In this study, the one-millimeter cell was compared with one marked 1.000 centimeters. Here too, the cells were used

TABLE XVIII

ABSORPTION DATA FOR EVALUATION OF THE RELATIVE OPTICAL PATH LENGTHS OF THE ONE MILLIMETER AND ONE CENTIMETER QUARTZ CELLS*

Wave-length(Å)	Absorbance Correction		Absorbance (Total)		Absorbance (Corrected)	
	1.000 mm. cell	1.000 cm. cell	1.000 mm. cell	1.000 cm. cell	1.000 mm. cell	1.000 cm. cell
2200	-0.078	-0.096	0.193	1.24	0.115	1.14
2250	-0.073	-0.089	0.142	0.800	0.069	0.711
2300	-0.074	-0.094	0.136	0.725	0.062	0.631
2350	-0.078	-0.106	0.157	0.918	0.079	0.812
2380	-0.085	-0.112	0.184	1.13	0.099	1.02
2400	-0.082	-0.113	0.199	1.29	0.117	1.18
2450	-0.080	-0.107	0.242	1.68	0.162	1.57

*The solution (absorbing medium) used in this study is discussed below.

individually to obtain readings, i.e., no reference cell was used. A solution considerably more concentrated in potassium chromate than that used for the preceding study served as the absorbing medium. Since attention here was directed primarily to the relative absorbances obtained with the two cells, no effort was made to prepare the solution quantitatively. As indicated by the data, the results appear quite good. The acceptance of the value, 1.000 mm., seems to be a valid one.

It will be noted that the above studies were limited to the short wavelength region of the ultraviolet. This range only was studied because, at the time, major concern was with the 2380Å position.

However, there seems to be no reason to doubt that comparable results would have been obtained at longer wavelengths.

Apparatus and Method for Preparation of Solutions

Special techniques were developed for preparing and transferring the solutions. The discussion which follows illustrates the procedure used in a typical run.

The second water distillation, as mentioned previously, was performed in a nitrogen atmosphere. A sketch of the apparatus is shown in Figure 18. (All joints, stoppers, and caps were of the ground-glass type: stopcocks A and B were of Teflon). The desired weighed quantities of sodium bromide and/or chloride were introduced into the empty volumetric flask before beginning the distillation. Stirring, provided by a magnetic stirrer (encased in glass), was necessary for solution of the salt and subsequent attainment of a homogeneous system. At the close of a distillation, the flask was removed from the distillation apparatus and the neck opening C immediately stoppered; nitrogen flow was maintained during this operation. The bromine was then introduced with the aid of a hypodermic syringe and micro-pipette. To accomplish this, the elbow-like piece D, leading upward from the neck of the volumetric flask, was partially lifted from the flask, the outlet E capped, and the bromine released into the flask. The piece D was then lifted clear of the flask and the neck opening F stoppered. With this procedure, the bromine was introduced against a continuous flow of nitrogen. The purpose for taking the above precautions was to prevent

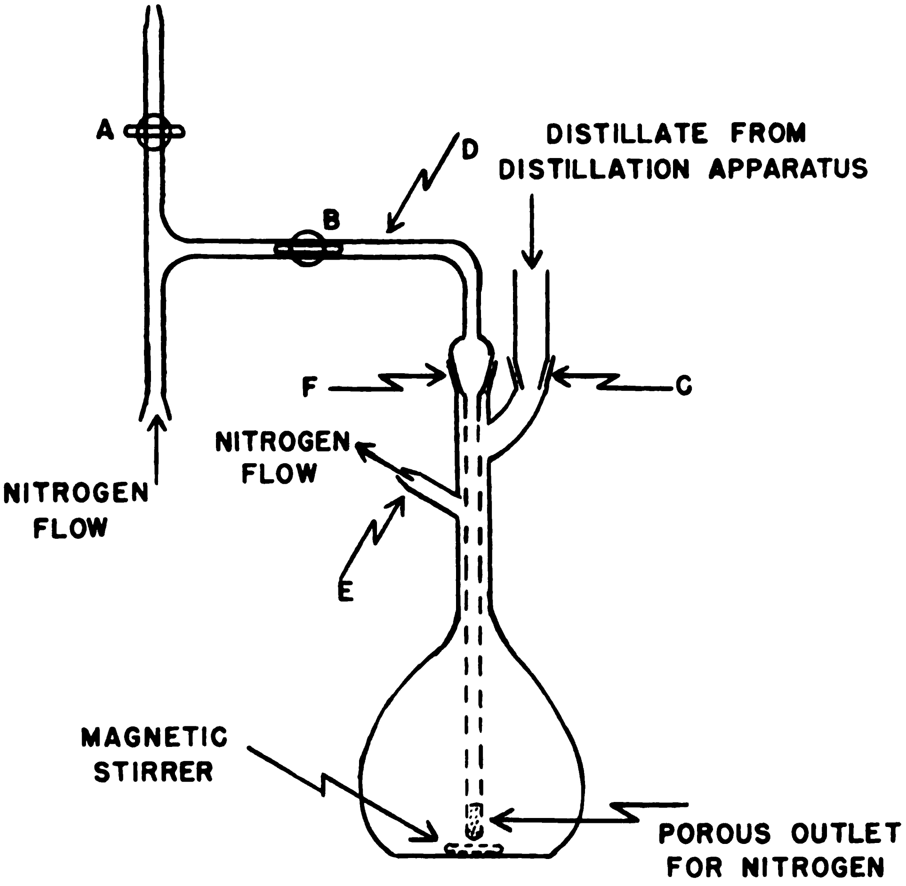


Figure 18. Apparatus for preparation of solutions.

entry of any carbon dioxide into the system. In the early studies, where the added salt content was very low, the increased hydrogen ion concentration occurring from the presence of any carbon dioxide might very well have affected the equilibrium concentration of bromide ion, and, consequently, the tribromide ion concentration. This procedure was used throughout the work. The flask itself had previously been completely covered with black photographic cloth, thus minimizing any effects produced by light.

Bromine was transferred from its storage vessel in the vacuum line by a vacuum distillation into a cold finger, from which it was removed with the aid of the hypodermic syringe and micro-pipette. The removal was made in a stream of nitrogen. Figure 19 shows the section of the vacuum system used for the distillation. The nitrogen flow was used, of course, only after the distillation, while removing the bromine.

It was found that Hooker Fluorolube (Grade MG) served satisfactorily as a lubricant for stopcocks and joints in the vacuum line. As would be expected, the more common greases, including the Dow-Corning silicone type, were subject to bromine attack, this effect being observed by the liberation of hydrogen bromide and darkening of the grease.

Apparatus and Method for Filling the Absorption Cell

A vacuum technique was utilized to fill the cell. Figure 20 is helpful in describing the procedure used. The diagram shows the elbow-like piece D refitted to the solution flask. The stem of the absorption cell was attached as shown to an intermediate section containing the

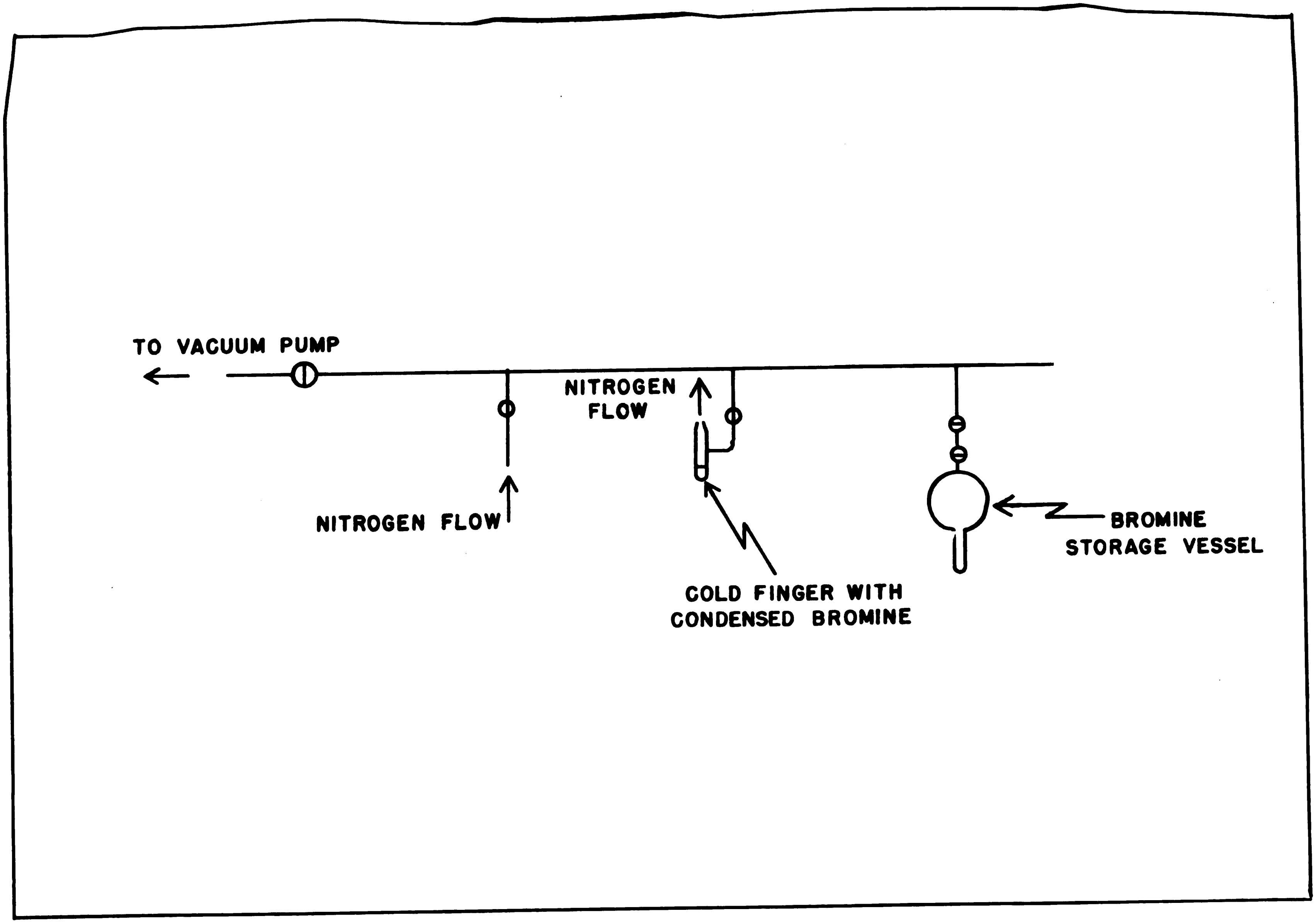


Figure 19. Manipulation of bromine in vacuum system.

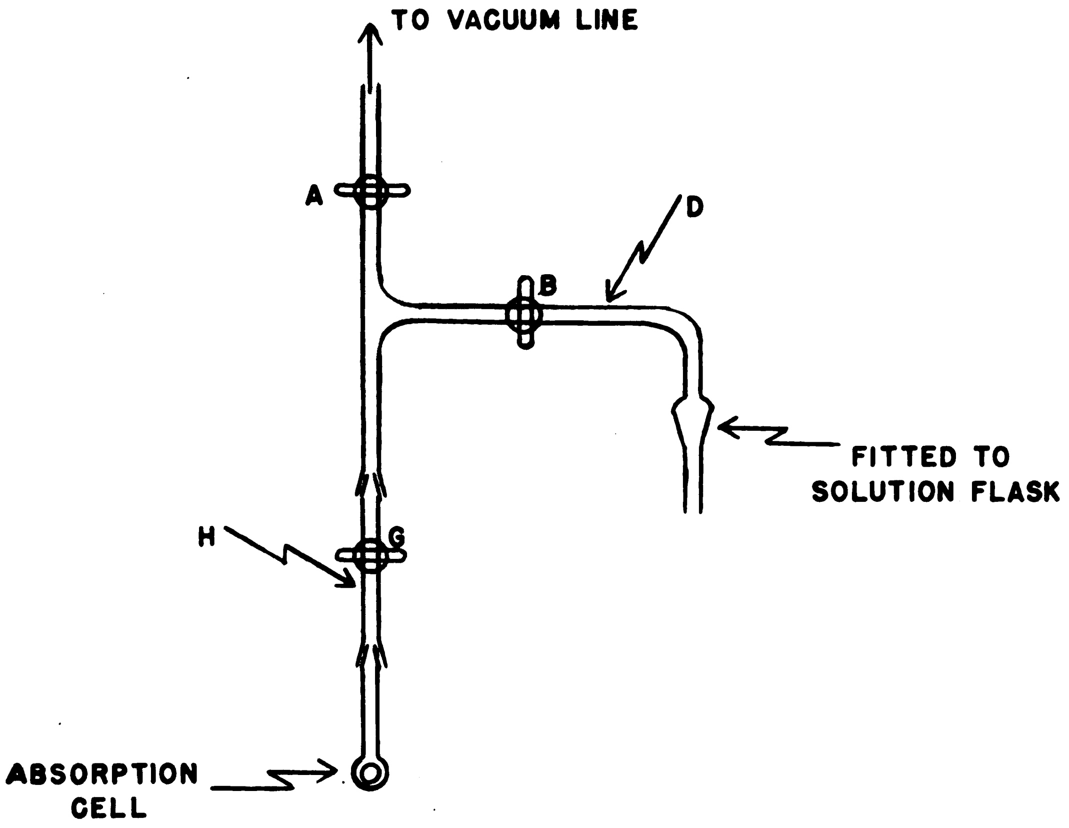


Figure 20. Apparatus for filling the absorption cell.

Teflon stopcock G. By proper manipulation of the stopcocks, the cell was first evacuated and then filled. The cell, together with the small section H containing the stopcock G (closed), was then removed as a unit and absorption readings taken. All regions of the apparatus, including the cell itself, were protected from light by careful masking with black cloth. Measurements with the spectrophotometer were made in a darkened room.

Determination of Volume of Solution and Volume of Solvent

The volume of solution used in each of the runs was determined as follows. (During the distillation, the volumetric solution flask was filled approximately to the 1000 cc. line etched on the neck of the container. However, upon removal of the tube leading nitrogen into the system, the level would be several centimeters lower. Hence, the final volume of solution, for each run, would be slightly less than 1000 cc.) For each run, the distance from the 1000 cc. marking to the meniscus formed by the salt solution was measured; the exact volume was then determined by making the necessary correction. This correction was determined directly from the data of a previously performed calibration of the volumetric flask. Table XIX shows the data obtained in the calibration, which was carried out with ordinary distilled water. The flask was first filled to the level for which the meniscus-to-line distance was equal to 4.5 cm. A burette was then used to add the increments of water corresponding to 0.1 cm. changes in meniscus height. It should be mentioned that the volume data for the runs were obtained

TABLE XIX

CALIBRATION OF VOLUMETRIC SOLUTION FLASK

Distance—Meniscus to 1000 cc. Mark (cm.)	Correction (ml.)	Distance—Meniscus to 1000 cc. Mark (cm.)	Correction (ml.)
0.1	0.2	2.4	5.9
0.2	0.5	2.5	6.2
0.3	0.7	2.6	6.4
0.4	1.0	2.7	6.6
0.5	1.2	2.8	6.8
0.6	1.5	2.9	7.1
0.7	1.7	3.0	7.4
0.8	1.9	3.1	7.7
0.9	2.2	3.2	8.0
1.0	2.5	3.3	8.3
1.1	2.7	3.4	8.7
1.2	2.9	3.5	9.0
1.3	3.1	3.6	9.3
1.4	3.3	3.7	9.6
1.5	3.6	3.8	10.0
1.6	3.8	3.9	10.3
1.7	4.0	4.0	10.6
1.8	4.3	4.1	10.9
1.9	4.6	4.2	11.2
2.0	4.9	4.3	11.5
2.1	5.1	4.4	11.9
2.2	5.4	4.5	12.2
2.3	5.6		

prior to the addition of bromine. The volume increase resulting from the bromine addition could be neglected since, in every case, less than 0.05 cc. of the liquid bromine was used. However, the volume of the glass-encased stirrer was considered and the necessary correction made. Table XX contains the detailed data for this phase of the work.

The use of the molality scale in our calculations required knowledge of the exact quantities of the solvent, water, used in each run. These data were obtained by preparing a second solution for each of those studied. In the preparation of these duplicate solutions, ordinary distilled water was added to the same weight of salt as used for the "run" solution, and dilution effected to the same volume as for the latter. In this instance, the volume of water was measured to obtain the desired data. Table XX also contains these data.

Analysis of Solutions for Bromine Content

Analysis of the salt solution for bromine content was carried out by titration with standard thiosulfate solution. Because the solutions were quite dilute in bromine (3×10^{-4} to 10^{-3} molar), it was necessary to use thiosulfate solution of about 0.01N. A rather large aliquot of the salt solution had to be used for each titration so as to require sufficiently large volumes of the titrating solution. For each run, three separate one hundred milliliter aliquots of the salt solution were titrated. The usual analytical method was employed—the aliquot was added to an acidic potassium iodide solution and the iodine thus liberated titrated using starch solution as an indicator. It was found

TABLE XX

DATA FOR COMPUTING SALT CONCENTRATIONS OF THE SOLUTIONS

Run No.	Distance (Meniscus to 1000 cc. Mark) (cm.)	Volume Correction (Preceding Column) (cc.)	Volume Correction (Stirrer) (cc.)	Volume of Solution (cc.)	Volume of Water (cc.)
138	1.8	4.3	2.8	992.9	992.6
139	1.8	4.3	2.8	992.9	992.5
140	2.0	4.9	2.8	992.3	991.3
142	2.8	6.8	3.0	990.2	989.0
143	3.4	8.7	3.0	988.3	987.1
144	3.4	8.7	3.0	988.3	986.6
145	3.8	10.0	3.0	987.0	982.7
146	3.7	9.6	3.0	987.4	979.1
147	2.0	4.9	3.0	992.1	971.7
148	3.7	9.6	3.0	987.4	959.8
149	3.7	9.6	3.0	987.4	971.9
150	4.5	12.2	3.0	984.8	960.1
151	3.7	9.6	3.0	987.4	931.6
152	4.3	11.5	3.0	985.5	923.2
155	1.8	4.3	2.2	993.5	980.7
156	1.8	4.3	2.2	993.5	976.3
157	1.2	2.9	2.2	994.9	987.1
158	0.0	0.0	2.2	997.8	992.8
159	1.3	3.1	2.2	994.7	990.8
160	3.5	9.0	2.2	988.8	978.1
161	1.4	3.3	2.2	994.5	985.3
162	1.9	4.6	2.2	993.2	984.2
163	1.6	3.8	2.2	994.0	985.0
164	1.7	4.0	2.2	993.8	981.1
165	1.7	4.0	2.2	993.8	974.0
166	2.4	5.9	2.2	991.9	985.0
167	2.8	6.8	2.2	991.0	984.0
168	2.0	4.9	2.7	992.4	976.1
169	2.5	6.2	2.7	991.1	972.9
171	4.0	10.6	2.7	986.7	977.1
172	3.1	7.7	2.7	989.6	980.9
173	4.0	10.6	0.9	988.5	970.7
174	2.2	5.4	0.9	993.7	973.7
175	4.2	11.2	0.9	987.9	970.8
176	3.8	10.0	0.9	989.1	971.0

that the volumes of titrating solution required for each of the three titrations were very nearly equal, the differences usually being of the order of a fraction of one per cent. Removal of the one hundred milliliter aliquots was made as rapidly as possible with a pipette. At all other times, the flask was tightly stoppered to prevent any loss of the volatile bromine. Of course, it would be expected that little loss would occur under any circumstances, since most of the bromine was present, under the existing equilibrium conditions, as the nonvolatile tribromide ion. The titration data for all of the runs considered in the preceding sections are shown in Table XXI.

Conversion of Activity Coefficients

As indicated previously (page 20), it was necessary to convert all activity coefficient values from the molality to the molarity scale. The conversion formulae were also briefly discussed in that section. Table XXII shows the results of all of the conversion calculations. For each run, the molality and molarity of the solution (with respect to salt concentration) is listed as well as the molar and molal activity coefficients for bromine and hydrobromic acid. The density of each solution is also included.

Several aspects of the calculation procedure should be pointed out. The simplest of the conversion formulae is, as shown previously,

$$f_{\pm} = (1 + 0.001mM_B)(d_o/d)\,\gamma_{\pm}$$

A value of 0.9970, the density of water at 25°C was used for d_0 (33).

TABLE XXI

ANALYSIS OF SOLUTIONS FOR BROMINE CONTENT

Run Number	Ml. of $Na_2S_2O_3$ Required for Titration of 100 cc. of Sol'n.				Normality of $Na_2S_2O_3$	Br_2 Conc. (moles/liter) (x 10^4)
	Tit. 1	Tit. 2	Tit. 3	Mean		
138	5.50	5.47	5.45	5.47	0.01076	2.94
139	7.20	7.20	7.23	7.21	0.01076	3.88
140	12.55	12.50	12.52	12.52	0.01076	6.74
142	8.80	8.74	8.70	8.75	0.01076	4.71
143	7.86	7.87	7.88	7.87	0.01076	4.24
144	6.96	6.76	6.80	6.84	0.01076	3.68
145	7.20	7.12	7.18	7.17	0.01076	3.86
146	7.15	7.15	7.18	7.16	0.01076	3.85
147	7.24	7.15	7.18	7.19	0.01076	3.87
148	7.12	7.12	7.14	7.13	0.01076	3.84
149	7.44	7.46	7.45	7.45	0.01076	4.01
150	7.66	7.60	7.63	7.63	0.01076	4.11
151	7.32	7.35	7.29	7.32	0.01076	3.94
152	7.14	7.22	7.17	7.18	0.01076	3.87
155	7.30	7.40	7.40	7.37	0.01060	3.91
156	7.54	7.43	7.55	7.51	0.01060	3.98
157	7.54	7.55	7.66	7.58	0.01060	4.02
158	7.48	7.42	7.50	7.47	0.01060	3.96
159	7.08	7.00	7.02	7.03	0.01060	3.73
160	7.71	7.71	7.74	7.72	0.01060	4.09
161	17.32	17.36	17.40	17.36	0.01060	9.20
162	16.50	16.53	16.53	16.52	0.01060	8.75
163	17.76	17.67	17.75	17.73	0.01060	9.40
164	16.63	16.52	16.65	16.60	0.01060	8.80
165	17.25	17.19	17.22	17.22	0.01060	9.12
166	15.88	15.82	15.88	15.86	0.01060	7.93
167	18.00	18.03	17.97	18.00	0.01060	9.54
168	16.92	16.88	16.98	16.93	0.01060	8.97
169	17.84	17.82	17.72	17.79	0.01060	9.43
171	3.73	3.85	3.80	3.79	0.01055	2.00
172	7.62	7.59	7.65	7.62	0.01055	4.15
173	7.68	7.75	7.75	7.73	0.01055	4.08
174	7.64	7.59	7.65	7.63	0.01055	4.03
175	7.50	7.58	7.50	7.53	0.01055	3.97
176	17.78	17.78	17.70	17.75	0.01055	9.37

TABLE XXII

SUMMARY OF ACTIVITY COEFFICIENT VALUES AND RELATED DATA

Run No.	Density of Solution (grams/cc.)	Molarity of Solution	Molality of Solution	Molar Activity Coef.		Molal Activity Coef.	
				Br_2(f)	HBr(f±)*	Br_2(γ)	HBr(γ±)*
138	0.998	0.009623	0.009626	1.002	∼1	1.002	∼1
139	0.998	0.01371	0.01372	1.003	∼1	1.003	∼1
140	0.999	0.03051	0.03054	1.007	0.857	1.006	0.855
142	1.001	0.04386	0.04391	1.009	0.834	1.009	0.834
143	1.001	0.04574	0.04580	1.011	0.832	1.009	0.831
144	1.004	0.08598	0.08613	1.019	0.804	1.018	0.803
145	1.013	0.1940	0.1949	1.045	0.771	1.040	0.768
146	1.030	0.4021	0.4055	1.095	0.762	1.086	0.756
147	1.061	0.8250	0.8425	1.211	--	1.186	--
148	1.083	1.108	1.140	1.296	--	1.260	--
149	1.053	0.6972	0.7082	1.172	--	1.154	--
150	1.082	1.064	1.091	1.279	--	1.248	--
151	1.162	2.147	2.275	1.679	--	1.586	--
152	1.365	4.187	4.470	2.638	--	2.474	--
155	1.027	0.7267	0.7361	1.204	--	1.189	--
156	1.036	0.9571	0.9738	1.279	0.799	1.257	0.785
157	1.019	0.5017	0.5057	1.135	0.749	1.126	0.743
158	1.012	0.3449	0.3466	1.090	0.744	1.085	0.740
159	1.004	0.1766	0.1773	1.047	0.768	1.043	0.765
160	1.029	0.7324	0.7404	1.203	0.767	1.190	0.759
161	1.019	0.5274	0.5323	1.144	0.748	1.133	0.741
162	1.012	0.4183	0.4221	1.114	--	1.104	--
163	1.103	0.4193	0.4231	1.115	--	1.105	--
164	1.025	0.6901	0.6990	1.194	0.761	1.178	0.752
165	1.041	1.079	1.101	1.322	0.825	1.296	0.801
166	1.021	0.5215	0.5252	1.139	--	1.131	--
167	1.021	0.5232	0.5269	1.140	0.746	1.132	0.741
168	1.034	0.9102	0.9254	1.263	0.791	1.243	0.779
169	1.045	1.134	1.156	1.336	0.831	1.312	0.816
171	1.027	0.5912	0.5969	1.158	--	1.146	--
172	1.022	0.5373	0.5420	1.144	--	1.134	--
173	1.042	1.028	1.047	1.283	--	1.260	--
174	1.041	1.089	1.111	1.324	--	1.298	--
175	1.034	0.9218	0.9381	1.268	--	1.246	--
176	1.037	0.9962	1.015	1.292	--	1.269	--

*The activity coefficient of hydrobromic acid was not required in all of the runs.

Knowing the volume and density of water, the weight of the salt(s), and the volume of the solution, the density of the solution, d, was then calculated from the expression,

$$d = \frac{(\mathrm{Vol.}_{H_2O})(d_0) + (\mathrm{Wgt.}_{\mathrm{salt(s)}})}{(\mathrm{Vol.}_{\mathrm{Total}})}$$

SUMMARY

An ultraviolet spectrophotometric investigation has been made of the formation equilibria of the tribromide and dibromochloride ions in aqueous solution at 25°C. The formation equilibrium constants were determined and compared with values obtained by other workers—in the past work, non-spectrophotometric methods were used almost exclusively. Molar extinction coefficients for the two ions have been determined at a number of wavelengths.

The system, water-bromine-sodium bromide, was chosen for the tribromide study, formation of the tribromide ion resulting from the reaction,

$$Br_2 + Br^- = Br_3^-$$

For this reaction, the equilibrium constant is

$$K_3 = \frac{a_{Br_3^-}}{a_{Br_2}\, a_{Br^-}} = \frac{(Br_3^-)}{(Br_2)(Br^-)} \; \frac{f_{Br_3^-}}{f_{Br_2}\, f_{Br^-}}$$

where the quantities in parentheses represent concentrations of the particular species, and a and f the activities and activity coefficients, respectively. Absorption of the trihalide ion is characterized by a very intense band with a peak at 2660Å. A graphical means was employed for treatment of the spectral and equilibrium data. The equilibrium constant, K_3, and the molar extinction coefficient at the band maximum,

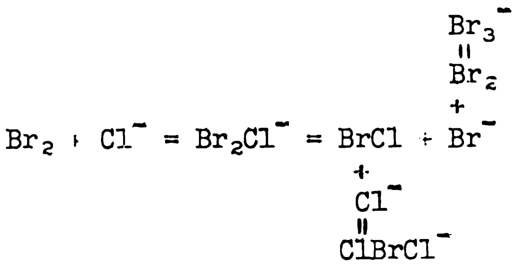
e_{2660}, were found to be 17.3 liter mole^{-1} and 3.46×10^4 respectively. Other workers, using distribution methods, have reported values for K_3 of approximately this value (11). Job, the only other investigator who has made a spectral determination, has reported a value 28.6 liter mole^{-1} (17).

To ascertain the effects of bromine hydrólysis on the tribromide ion formation, several methods of calculation were tried. With solutions dilute in sodium bromide, the hydrolysis reaction,

$$H_2O + Br_2 = HOBr + H^+ + Br^-$$

could conceivably, because of bromide formation and bromine consumption, affect the tribromide equilibrium. However, even in solutions as dilute as 0.01 molar in added bromide (bromine concentrations varied from 10^{-4} to 10^{-3} molar), hydrolysis was shown to be virtually completely suppressed.

The dibromochloride ion study proved to be much more complicated. For this study, the system, water-bromine-sodium chloride, was chosen. Ultraviolet absorption for this system is characterized by an intense band with a peak at 2380Å. The formation reaction and equilibrium constant expression are analogous to those for the tribromide ion. The results obtained, were, however, inconsistent with the rather concordant results in the literature. The equilibrium constant for this system was found to be 0.567 in contrast with a literature value of 1.39 liter mole^{-1} (20). Complicating side-reactions are believed to play a role in this system. A possible reaction scheme may be the following:



$$\begin{array}{ccccccc}
 & & & & & & \mathrm{Br_3^-} \\
 & & & & & & \| \\
 & & & & & & \mathrm{Br_2} \\
 & & & & & & + \\
\mathrm{Br_2} + \mathrm{Cl^-} & = & \mathrm{Br_2Cl^-} & = & \mathrm{BrCl} & + & \mathrm{Br^-} \\
 & & & & + & & \\
 & & & & \mathrm{Cl^-} & & \\
 & & & & \| & & \\
 & & & & \mathrm{ClBrCl^-} & &
\end{array}$$

Since the addition of bromide would retard these side effects, it was decided to study the system, water-bromine-sodium chloride-sodium bromide. The analysis was thereby complicated since the simultaneous equilibria,

$$Br_2 + Cl^- = Br_2Cl^-$$

and

$$Br_2 - Br^- = Br_3^-$$

had to be considered. In addition, the spectra were more complex since the ultraviolet absorption bands of the two ions overlap. Nevertheless, by considering the absorption of both ions at several wavelengths, a method of solution was developed. A value of 1.39 liter mole^{-1}, in very good agreement with the reported literature values, was calculated for the equilibrium constant. The method also led to a characterization of the dibromochloride ion absorption band for the spectral region studied. At the wavelength of maximum absorption, 2430Å, the molar extinction coefficient was estimated to be 2.19×10^4.

A qualitative study was made of the water-bromine system. This study was undertaken to elucidate the short wavelength band exhibited by this system in the approximate range, 2550 to 2650Å. Numerous investigators have reported the presence of the band (2) but no satisfactory explanation has been presented as to what may be the absorbing species. The study was necessarily qualitative because of the instability, as indicated by the spectral changes, of the very dilute bromine solutions. Nevertheless, two distinct types of changes, one occurring in the dark and the other in the light, were recognized. In both cases, the changes consisted of a shifting of the band toward longer wavelengths; in the dark, however, the shift was accompanied by a decrease in band intensity whereas an increase in intensity occurred in the "light" study. To explain the dual behavior, it was assumed that the tribromide ion is present in the system, and that the absorption band under consideration is produced principally by the trihalide absorption. The tribromide ion would be formed by the reaction of bromine and bromide ion, the latter produced by the hydrolysis of bromine. Hypobromous acid, also produced in the hydrolysis reaction, also absorbs in this region of the spectrum. The absorption of the tribromide ion and of the acid, together with the changes produced by the "light" and "dark" decomposition of the acid, can lead to the plausible explanation presented and thus account for the observed spectrum and its time-dependence.

As mentioned at the beginning of the thesis, attempts to obtain a suitable solvent for the initially proposed photochemical study were not successful. However, several interesting spectral phenomena were observed in these early studies, and these will be discussed in this section. The order of presentation will be similar to that followed in Part I. Pertinent background material from the literature will first be reviewed. A discussion of our findings will then follow. Finally, experimental aspects of the studies will be considered.

HISTORICAL SUMMARY

Pertinent Past Studies

Popov and Swenson (18) have studied the systems, acetonitrile--tetrabutylammonium tribromide and ethylene dichloride-tetrabutylammonium tribromide. These investigators obtained quantitative data on the absorption spectra of the tribromide ion in each of the solvents. In acetonitrile, the absorption maximum occurs at 2690Å; the molar extinction coefficient was estimated to be 55,000. In ethylene dichloride, the absorption maximum is located at 2730Å and the extinction coefficient was calculated to be 54,000.

The tribromide ion is formed directly from the complete dissociation of the tribromide salt. Because polyhalide ions themselves dissociate in acetonitrile, it was found necessary to add an excess of tetrabutylammonium bromide to the solutions to suppress the further dissociation. Since the simple halides show no appreciable absorption at the wavelength investigated, no error was thereby introduced.

PART II

Bromine Complexing in Several Organic Solvents

Another series of studies that seem to be related to those in the present investigation are those made by Keefer and Andrews (34). These workers, in addition to others, have clearly shown that bromine forms a 1:1 complex with a large number of compounds. For example, they have studied such systems as bromine-methyl iodide in carbon tetrachloride, bromine-n butyl bromide in the same solvent, iodine-t butyl chloride in heptane, and others. Using the formation equilibrium expression,

$$X_2 + RY = RYX_2$$

with equilibrium constant,

$$K = \frac{(RYX_2)}{(X_2)(RY)}$$

together with the spectral data, it was possible to calculate the equilibrium constant for each system. The concordant results obtained by making the calculations at different wavelengths seemed to leave little doubt as to the nature of the phenomena involved.

Keefer and Andrews, in addition to other independent workers, have stated that in such systems, the halogen molecule functions as an electron acceptor. A structure for the complex based on a resonance hybrid of $R:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\overset{\cdot\;\;\cdot}{X}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$ and related electronic forms seems reasonable. This belief is further supported by noting that the equilibrium constants for the formation of the alkyl iodide-iodine complexes in heptane solution decrease with change in the structure of the alkyl group in the order, t-butyl > i-propyl > ethyl > methyl. This stability series is the reverse of that for the relative inductive effects of the alkyl groups, and also the reverse of the effect which would result from steric factors.

The spatial geometry of the complexes may be similar to that proposed by Pauling (35) for trihalide ions. The trihalide ion has been shown, by X-ray methods, to be linear in crystals of alkali compounds. It is probable that the configuration is that of a trigonal bipyramid with halogen atoms at the two pyramidal apices and the three unshared electron pairs in the equatorial plane.

Still another series of studies pertinent to the present one is a very recent one by Popov and Deskin (36) in which various iodine halides, in the solvent, acetonitrile, were considered. These workers found that iodine monochloride, iodine bromide, and iodine each form 1:1 complexes with acetonitrile. Both their conductance and spectrophotometric data indicate that a definite change occurs with time for each of the systems. The slowly increasing conductance and accompanying absorption changes were interpreted as being associated with a slow transition of the "outer complex," CH_3CNIX, to the "inner complex," $(CH_3CNI)^+ X^-$. One other very interesting aspect of the system, acetonitrile-iodine, is that the triiodide ion is formed. The presence of this ion is indicated by its ultraviolet absorption, characterized by two intense absorption peaks, one at 3600Å and the other at 2910Å.

THE PRESENT INVESTIGATION--RESULTS AND DISCUSSION

The Cyclohexane-Bromine System

Despite the ideal ultraviolet transparency of the cyclohexane, the system formed with bromine was not found sufficiently stable to warrant its use. The instability was observed by studying the intensity of the bromine absorption with time at the wavelength of maximum bromine absorption, 4200Å. Studies were made in the dark as well as under normal conditions of room lighting. Since this cycloparaffin should be relatively inert to bromine attack, it must be concluded that all traces of reactive impurities were not removed in the purification. As was stated previously, attempts to purify this solvent were not extensive since it was believed, at the time, that another solvent, suitable for our purposes, would easily be found.

The Acetonitrile-Bromine System

As indicated previously, acetonitrile did not prove to be useful as a solvent primarily because of the intense ultraviolet absorption exhibited by this system. The absorption maximum of this band, which is shown in Figure 21, is at approximately 2700Å. Popov's spectral investigation (18) of tetrabutylammonium tribromide in acetonitrile suggested that the tribromide ion may be the absorbing species; both the intensity (qualitatively) and location of the bands in the two systems are in agreement. In addition, it will be recalled that in the system, acetonitrile-iodine, Popov reported the presence of the

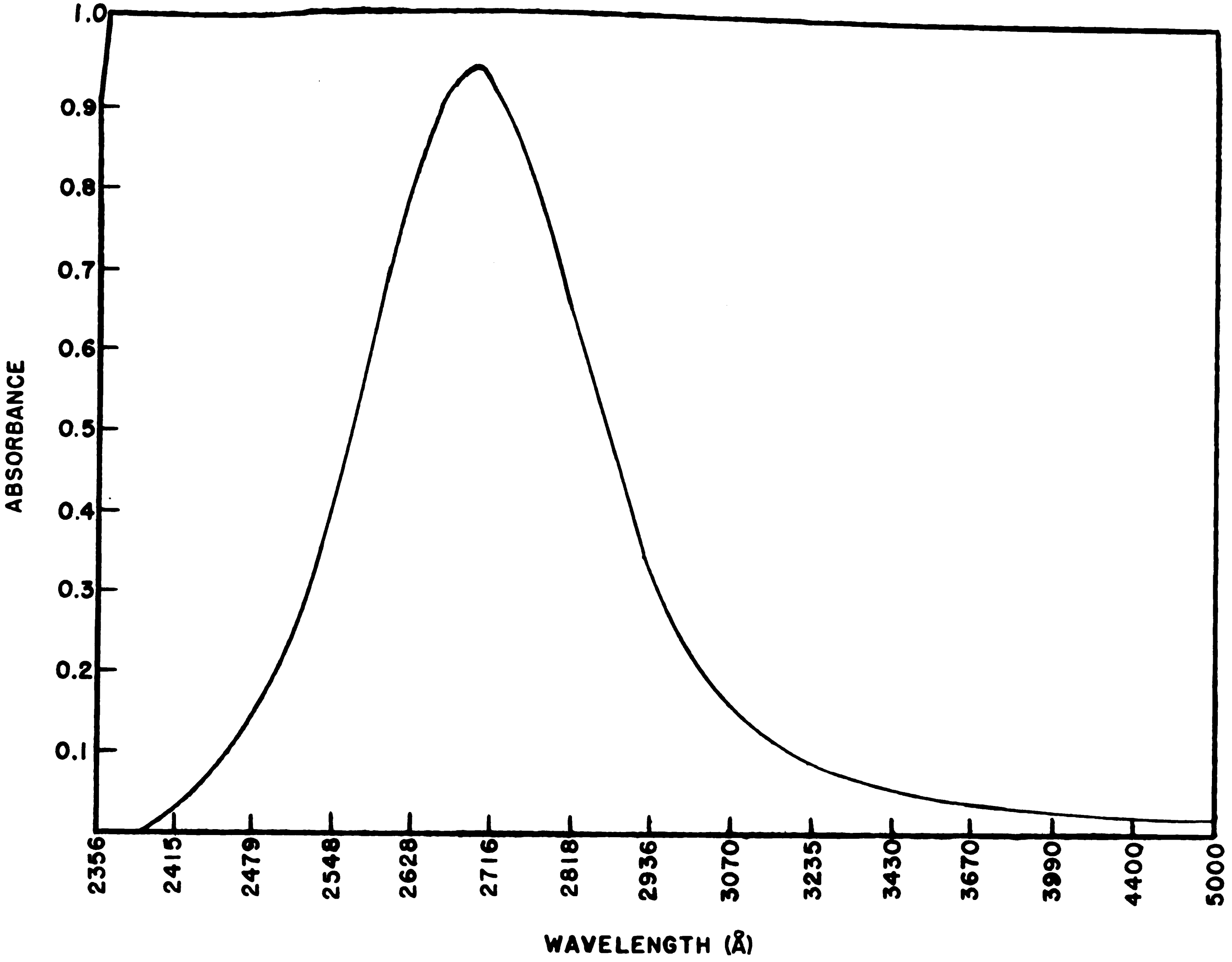


Figure 21. Ultraviolet absorption spectrum of a dilute solution of bromine in acetonitrile.

triiodide ion (36). It would appear that in the analogous system, acetonitrile-bromine, the tribromide ion might well be present.

The tribromide ion in the present system could be formed as follows: the solvent would first interact with the bromine to form a 1:1 complex,

$$CH_3CN + Br_2 = CH_3CNBr_2$$

Dissociation of the complex in the fairly highly-ionizing acetonitrile (dielectric constant = 37.5 at 20°C) might then proceed as follows:

$$CH_3CNBr_2 = (CH_3CNBr^+Br^-) = CH_3CNBr^+ + Br^- \qquad (2)$$

The tribromide ion could then be formed in the usual manner, i.e.,

$$Br_2 + Br^- = Br_3^- \qquad (3)$$

When studied as a function of time, the spectra indicated that the system underwent a gradual change. The nature of these changes seemed to be dependent on the manner in which the solution was prepared. When no dilution was involved (bromine added directly to the solvent), the intense ultraviolet band exhibited a gradual increase in intensity. In all cases, this increase was observed on the band shoulder, since the absorption at the maximum was beyond the absorbance range of the instrument. However, when such a solution was diluted so as to observe the absorption at the peak (2700Å), the intensity showed a slow decrease with time.

Attempts to explain the dual behaviour of the system on the basis of the proposed equilibria (1), (2), and (3) failed. An alternative explanation which seems in better agreement with the observed behaviour involves the two principal equilibria:

$$CH_3CN + Br_2 = \left[\begin{array}{c} CH_3CNBr_2 \\ \| \\ CH_3CNBr^+Br^- \end{array}\right] \qquad (1)$$

and

$$2\left[\begin{array}{c} CH_3CNBr_2 \\ \| \\ CH_3CNBr^+Br^- \end{array}\right] = CH_3CNBr^+Br_3^- + CH_3CN \qquad (4a)$$

or

$$\left[\begin{array}{c} CH_3CNBr_2 \\ \| \\ CH_3CNBr^+Br^- \end{array}\right] + Br_2 = CH_3CNBr^+Br_3^- \qquad (4b)$$

The bracketed equilibria indicate that no distinction has been made between the "outer complex" and the "inner complex" ion pair in the reactions considered here. Equilibrium (1) is postulated to be rapid, with (4a) or (4b) slower equilibria. These may be accompanied, to a lesser extent, by the slow ionizations,

$$CH_3CNBr^+Br^- = CH_3CNBr^+ + Br^- \qquad (5)$$

$$CH_3CNBr^+Br_3^- = CH_3CNBr^+ + Br_3^- \qquad (6)$$

$$Br_3^- = Br_2 + Br^- \qquad (7)$$

The observed tribromide absorption is attributed principally to the ion pair, $CH_3CNBr^+Br_3^-$, in accord with the ion-pairing tendencies in many

non-aqueous solvents, and in accord with the tendency of ions involved in ion pairs to show absorption very similar to that of the free ions.

The slow attainment of equilibrium according to (4a) or (4b) would explain the gradual changes in absorption intensity. In a freshly prepared solution (4a) or (4b) would slowly form the tribromide ion pair, with increasing absorbance as a function of time. Dilution would drive (4a) or (4b) towards the left so that the tribromide ion pair concentration immediately after dilution would be excessive, and its absorbance would decrease as the new equilibrium is approached.

The Ethylene Dichloride-Bromine System

Our studies of the system, ethylene dichloride-bromine, clearly indicate that some type of interaction results. It was observed that a very intense new ultraviolet absorption occurs upon mixing the reactants; the long wavelength edge of the band is in the vicinity of 2500Å. Figure 22 shows the absorption of the solvent alone and also of a very dilute solution of bromine in the solvent. Unfortunately, the limited transparency of the solvent would not permit the whole of the band to be observed. It seems probable that complexing may be involved. As with the preceding examples of complex formation, the electrophilic bromine could form a loose "donor acceptor" or charge-transfer" type bond with the nucleophilic chlorine of the solvent molecule. A literature search revealed that no thorough studies have been previously made with this system. Buckles and Mills (37) concluded that complexing does not occur and justified their conclusion on the

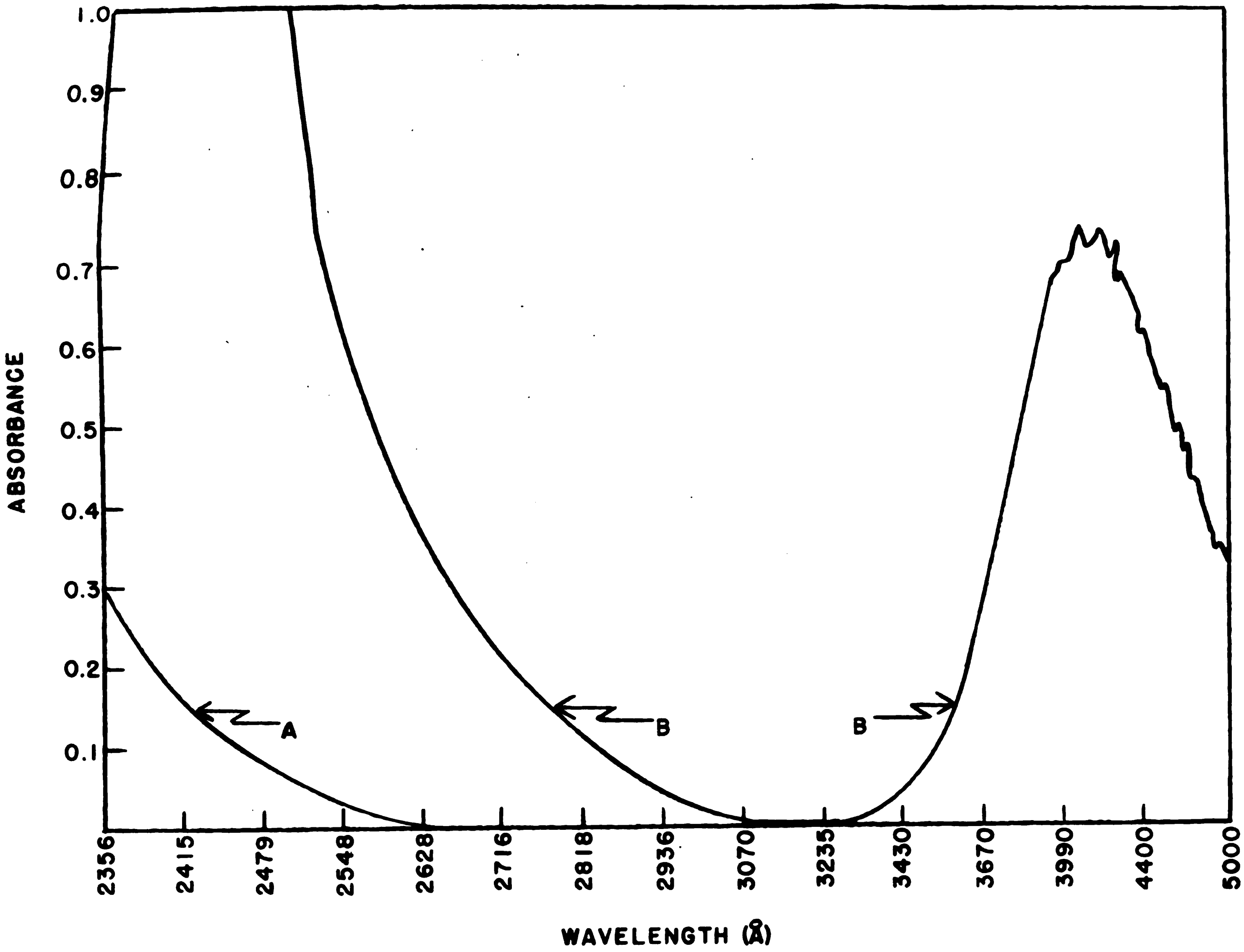


Figure 22. Ultraviolet absorption spectra of ethylene dichloride (Spectrum A) and of a dilute solution of bromine in ethylene dichloride (Spectrum B).

basis of the relatively non-polar nature of the ethylene dichloride molecule. However, it appears that their studies were not extended to sufficiently short wavelengths; the absorption would therefore not have been noted. Another factor which may have caused these investigators to fail to observe the intense absorption might be concerned with solvent purity. We have found that with extensive purification it was possible to extend the ultraviolet cut-off of the pure solvent down to approximately 2280Å. The purified ethylene dichloride used by Popov (18) for his tetrabutylammonium halide studies was transparent down to about 2350Å. It may very well be that the solvent used by Buckles had a cut-off too near the region of absorption to have detected the latter.

The possibility of the reaction of bromine with the solvent was considered but does not seem very probable. Study of the visible absorption band of bromine with time indicated no depletion of the halogen. In addition, any reaction would very likely have resulted in the formation of hydrogen bromide. The ultraviolet absorption of gaseous hydrogen bromide consists of a primary band with absorption maximum at 2870Å and a secondary band with its maximum at 3480Å (38).

The Fluorocarbon-Bromine Systems

A few fluorocarbons were also tried as possible solvents. Those examined were Fluorolube (Hooker - F. S.), perfluorokerosene (Du Pont), and 2, 2, 3 trichlorheptafluorobutane (Hooker). The ultraviolet cut-off values for these compounds were found to be 2850, 3280, and 2500Å, respectively. The rather high cut-offs precluded their use with bromine

unless purification improved their ultraviolet transparency. However, because of the advantages of using solvents more readily available, purification was not attempted.

EXPERIMENTAL

Source and Purification of Reagents

Cyclohexane

The cyclohexane (Eastman) displayed a weak absorption at approximately 2900Å with a somewhat stronger band at about 2600Å. Purification was attempted by passing the liquid through a 1-meter, 40-mm. i.d. column packed with silica gel (39). This procedure resulted in a product with a cut-off of approximately 2100Å as compared with one of approximately 2200Å for the unpurified liquid. The absorption at 2900Å displayed by the latter was virtually eliminated by this procedure.

Acetonitrile

Several purification schemes were tried for the acetonitrile (Matheson, Coleman, and Bell). The unpurified solvent, with a cut-off at 2430Å, showed an absorption in the 2600-2900Å region. A purification method used by Wawzonek and Runner (40) proved to the most efficient of those tried. For a typical purification run, the procedure was as follows. Five hundred milliliters of the solvent was fractionally distilled. A middle fraction of 440 cc. was then added to the same volume of saturated potassium hydroxide solution and the mixture agitated for a period of six hours. After separation from the aqueous phase, an ample supply of sodium carbonate was added to the organic phase and this mixture stirred for two hours. The separated organic phase was then distilled from phosphorous pentoxide. A middle fraction of 300 cc. showed excellent ultraviolet transparency, the cut-off being in the range 1990-2070Å.

Ethylene Dichloride

Purification of the ethylene dichloride was also attempted by various means. Eastman solvent (White Label) displayed appreciable absorption in the 2700-2900Å region with a cut-off value of approximately 2470Å. Traces of benzene also appeared to be present as indicated by slight absorption at 2610 and 2550Å, these being superimposed on the main spectrum.

Of the various schemes attempted for purification, the following appeared to be most effective. Quantities of the reagents used are included, although they are probably not critical. Four hundred milliliters of the solvent, 4 cc. of bromine, and 5 grams of iron filings were mixed in a liter flask, and the mixture was then refluxed overnight. The solution was then fractionally distilled and the spectrum of each fraction obtained. Cut-off values for all fractions in the first 320 cc. of distillate were in the range 2380-2420Å. Ninety milliliters from the middle fractions was then mixed with 1 cc. of bromine and this mixture was refluxed overnight. Fractional distillation of the latter followed by spectral studies of the fractions showed that the initial 60 cc. of distillate had cut-off values in the range 2270-2290Å. The addition of the iron catalyst was necessary to remove the benzene present, the benzene being brominated with the catalyst present--

separation was subsequently readily effected in the distillation step. The boiling points of ethylene dichloride and benzene are 83.5 and 80.1°C, respectively; separation by fractional distillation would have been extremely difficult. On the other hand, the high boiling point of the brominated product, bromobenzene, effects easy separation. In runs with bromine present, but in the absence of the iron catalyst, the benzene band was observed in its entirety with the fractions obtained in the subsequent distillation. Refluxing of the solutions was carried out in a lighted hood, the light being furnished by two 200-watt tungsten lamps. It was noted that best results were obtained with a straight reflux condenser--for some inexplicable reason, use of a spiral reflux condenser repeatedly resulted in a less transparent solvent.

Since the purification method described results in a solvent with excellent ultraviolet transparency, it should serve satisfactorily as a general method for obtaining spectroscopic-grade ethylene dichloride. The purification method is based upon the following crude, but rather fruitful, analogy: groups displaying chromophoric behaviour in the near ultraviolet region of the spectrum tend also to be reactive with bromine. The high boiling points of the resultant brominated products facilitate their removal by distillation.

Apparatus

All of the spectral studies considered in this section of the thesis were made with a Beckman DK-2 recording spectrophotometer. A pair of one-centimeter quartz cells was used throughout. The systems were studied at room temperature.

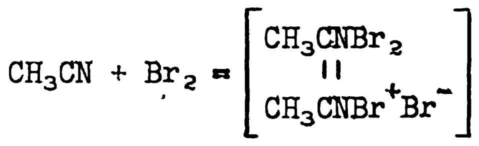
SUMMARY

The studies considered in this section of the thesis were a direct consequence of attempts to obtain a solvent which is both inert to bromine and transparent throughout the ultraviolet region of the spectrum. A solvent with these characteristics was desired for another investigation. Although a satisfactory solvent was not found, the studies revealed several interesting spectral phenomena. These findings are presented. The solvents investigated are cyclohexane, acetonitrile, and ethylene dichloride, the latter two being studied rather extensively. Several fluorocarbon compounds were also tried as possible solvents.

Despite the ideal ultraviolet transparency of the cyclohexane, the system formed with bromine was not found to be sufficiently stable. All traces of reactive impurities were apparently not removed in the purification.

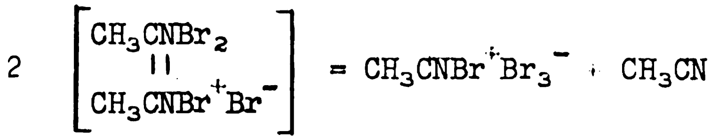
Acetonitrile did not prove to be a satisfactory solvent, primarily because of the intense ultraviolet absorption exhibited by the system, acetonitrile-bromine. The absorption maximum of this band is at approximately 2700Å. Popov's spectral investigation of tetrabutylammonium tribromide in acetonitrile (18), a study in which the spectral characteristics of the tribromide ion in this solvent were defined, suggested the presence of this ion in the system, acetonitrile-bromine. Both the intensity (qualitatively) and location of the bands in the two systems are in agreement. Other evidence also indicate that the tribromide ion is the absorbing species. For example, Popov has found that the triiodide ion is produced in the system, acetonitrile-iodine (36).

The intense band formed in the acetonitrile-bromine system was found to undergo very slow changes with time. Two distinct trends were recognized; when the solution was prepared directly, i.e., bromine added to the acetonitrile, the 2700Å band underwent a slow increase in intensity--when the solution was prepared by dilution, the band intensity slowly decreased. Plausible explanations have been presented for the mechanism of tribromide ion formation as well as for the changes described above. The following two equilibria have been postulated to explain the observed results:



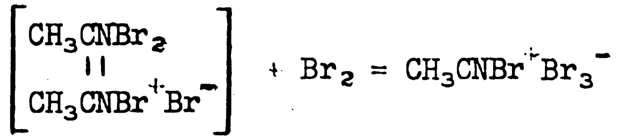
$$CH_3CN + Br_2 = \left[\begin{array}{c} CH_3CNBr_2 \\ \parallel \\ CH_3CNBr^+Br^- \end{array}\right] \qquad (1)$$

and



$$2\left[\begin{array}{c} CH_3CNBr_2 \\ \parallel \\ CH_3CNBr^+Br^- \end{array}\right] = CH_3CNBr^+Br_3^- + CH_3CN \qquad (2)$$

or



$$\left[\begin{array}{c} CH_3CNBr_2 \\ \parallel \\ CH_3CNBr^+Br^- \end{array}\right] + Br_2 = CH_3CNBr^+Br_3^- \qquad (2a)$$

The observed tribromide ion absorption is attributed to the ion pair, $CH_3CNBr^+Br_3^-$. Considering (1) as a rapid and (2) or (2a) as slower equilibria, the time-dependent spectral changes can be explained.

Ethylene dichloride, after extensive purification, was found to be inert to bromine. In addition, the purified solvent alone is fairly transparent in the ultraviolet region, the cut-off value being approximately 2280Å. However, a solution of bromine in ethylene dichloride exhibits an intense absorption in the region below 2500Å. Since only the long wavelength edge of the band could be observed, it must be assumed that the band peak is located at a shorter wavelength than that at which the solvent itself begins to absorb. It is probable that the 1:1 complex, $ClCH_2CH_2ClBr_2$, is formed in this system; this species could account for the absorption.

A purification method for ethylene dichloride was devised which should serve satisfactorily as a general means for obtaining a spectroscopic grade of the solvent. The purified ethylene dichloride is more transparent than the product used by other workers. The method involved two treatments of the solvent with bromine, followed, in each case, by a fractional distillation. With the first treatment, an iron catalyst was used to promote bromination of trace impurities; in the second, a light bromination was utilized. The relatively higher boiling points of the brominated products facilitated separation by the subsequent distillations.

Several fluorocarbons were also tried as possible solvents. However, the rather poor transparency of those investigated precluded their use with bromine. Purification was not attempted because of the advantages of using solvents more readily available.

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