Interaction of Quaternary Ammonium Ions with the Ions of Bromocresol Green

Daniel Yue-King Chan
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INTERACTION OF QUATERNARY AMMONIUM IONS
WITH
THE IONS OF BROM CRESOL GREEN

by

Daniel Yue-King Chan

A Thesis submitted to Faculty of the Graduate School
of Loyola University in Partial Fulfillment of
the Requirements for the Degree of
Master of Science

June
1967
LIFE

Daniel Yue-King Chan was born in Hong Kong, China, December 15, 1941. He was graduated from Hope College, Holland, Michigan, U.S.A., June, 1964, with the degree of Bachelor of Science.

In September, 1964 he began further studies in chemistry at Miami University, Oxford, Ohio. In September, 1965 he began graduate studies at Loyola University in the Department of Biochemistry and Biophysics holding the positions of research assistant and teaching assistant from September 1965 to June, 1967.
ACKNOWLEDGEMENT

The author wishes to extend to Dr. Norma C. Melchior the deepest appreciation and gratitude for his invaluable, encouraging, enlightening guidance, as well as his kindness and infinite support in the preparation of this work.
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>7</td>
</tr>
<tr>
<td>III. RESULTS</td>
<td>14</td>
</tr>
<tr>
<td>IV. DISCUSSION</td>
<td>28</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>40</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>41</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. COMPOSITION OF BASIC SOLUTIONS</td>
<td>10</td>
</tr>
<tr>
<td>II. COMPOSITION OF ACID SOLUTIONS</td>
<td>10</td>
</tr>
<tr>
<td>III. THE EFFECT OF TETRA-n-BUTYLMAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY SOLUTIONS OF BROM CRESOL GREEN</td>
<td>16</td>
</tr>
<tr>
<td>IV. THE EFFECT OF TETRA-n-BUTYLMAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY DINEGATIVE ION OF BROM CRESOL GREEN</td>
<td>23</td>
</tr>
<tr>
<td>V. THE EFFECT OF TETRA-n-BUTYLMAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY DINEGATIVE ION OF BROM CRESOL GREEN*</td>
<td>24</td>
</tr>
<tr>
<td>VI. THE EFFECT OF TETRA-n-BUTYLMAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY MONONEGATIVE ION OF BROM CRESOL GREEN</td>
<td>25</td>
</tr>
<tr>
<td>VII. THE EFFECT OF TETRA-n-BUTYLMAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY MONONEGATIVE ION OF BROM CRESOL GREEN</td>
<td>26</td>
</tr>
<tr>
<td>VIII. DENSITIES OF BASIC AND ACID SOLUTIONS</td>
<td>27</td>
</tr>
<tr>
<td>IX. FORMATION CONSTANTS FOR THE COMPLEX BETWEEN TETRA-n-BUTYLMAMMONIUM IONS AND THE IONS OF BROM CRESOL GREEN</td>
<td>33</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>THE EFFECT OF TETRAALKYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY SOLUTIONS OF BROM CRESOL GREEN</td>
<td>15</td>
</tr>
<tr>
<td>2.</td>
<td>THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY BASIC SOLUTIONS OF BROM CRESOL GREEN</td>
<td>18</td>
</tr>
<tr>
<td>3.</td>
<td>THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY ACID SOLUTIONS OF BROM CRESOL GREEN</td>
<td>19</td>
</tr>
<tr>
<td>4.</td>
<td>THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY BASIC SOLUTIONS OF BROM CRESOL GREEN</td>
<td>21</td>
</tr>
<tr>
<td>5.</td>
<td>THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY ACID SOLUTIONS OF BROM CRESOL GREEN</td>
<td>22</td>
</tr>
<tr>
<td>6.</td>
<td>DETERMINATION OF EQUILIBRIUM CONSTANT OF THE 1:1 COMPLEX BETWEEN TETRA-n-BUTYLAMMONIUM ION AND AN ION OF BROM CRESOL GREEN</td>
<td>31</td>
</tr>
<tr>
<td>7.</td>
<td>DETERMINATION OF EQUILIBRIUM CONSTANT OF THE 1:1 COMPLEX BETWEEN TETRA-n-BUTYLAMMONIUM ION AND AN ION OF BROM CRESOL GREEN</td>
<td>32</td>
</tr>
<tr>
<td>8.</td>
<td>DETERMINATION OF EQUILIBRIUM CONSTANT OF THE 1:1 COMPLEX BETWEEN TETRA-n-BUTYLAMMONIUM ION AND THE IONS OF BROM CRESOL GREEN</td>
<td>34</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Much attention has been focused on the color changes of indicators due to a displacement of the acid-base equilibrium in favor of one of the prevailing forms. In a study of the effects of anionic, cationic and non-ionic detergents on a large number of indicators, Hartley (1934) used long-chain quaternary ammonium salts which give soap-like solutions containing aggregates of long-chain ions. The salts produced a similar effect on the color change as did the soaps. He found that the color change was due to the interaction of electric charges on the indicator and the added long-chain ions which acted like an acid if the aggregates carried negative charges, and acted like a base if they carried positive charges. Other than the electrostatic forces, proposals of chemical combination were suggested (Miss Mersol, 1961) as a result of the investigation of spectra of sulfonphthalein indicators.

Auerbach (1943) and Ballard (1954) determined the concentration of long-chain quaternary ammonium salts by photometric methods which were based on the measurement of the indicator extracted by means of the quaternary ammonium compound. While using brom thymol blue and chloroform as the extracting solvent, Ballard interpreted the fact that the slopes of the calibration curves expressed as extinction/concentration (mg/ml)
were directly proportional to the number of quaternary nitrogen atom per molecule, as evidence of a one-to-one combination between the molecules of indicator and quaternary ammonium ion.

Zutrauen and Ter-Minassian (1955) studied the color change in brom phenol blue in the presence of some quaternary ammonium salts. Various concentrations of solutions of lauryl-, myristyl- and cetyltrimethylammonium bromide ($C_{12}$, $C_{14}$, $C_{16}$) were studied in the same amount of brom phenol blue. The concentration of indicator was $7.5 \times 10^{-6}$ M. The optical density at the maximum (592.0 mu) decreased as the concentration of the quaternary ammonium salts increased. It began to rise toward a new peak at about 605.0 mu when the concentration was greater than $9.07 \times 10^{-5}$ molar.

The author suggested that only one kind of complex was formed in these experiments and that micelle formation was not a factor in the color change observed. Experiments in which the addition of KCl was shown to be without effect on the concentration of quaternary ion at which a minimum absorbance of brom phenol blue was observed, support their conclusion.

Experiments with brom cresol green and cetyltrimethylammonium ion (Mersol, 1961) support some of the conclusions of Zutrauen and Ter-Minassian, but not all. For example Zutrauen and Ter-Minassian state that the small precipitate seen does not affect the results. When Mersol removed the precipitates by centrifugation, she demonstrated that, in both acid and basic
solutions, the remaining indicator had an unchanged absorption maximum. In acid solution, $1 \times 10^{-4}$ M quaternary ammonium ion had removed substantially all the indicator from solution ($1.7 \times 10^{-6}$ M). A similar concentration removed 90% of the indicator ($8.9 \times 10^{-7}$ M) from basic solution. Higher concentrations (0.6 and 1.0 millimolar) gave clear solutions from which no precipitate could be removed. This indicates that the compounds which precipitated, dissolved in excess of quaternary ammonium ion. Since the concentrations which dissolved all the indicator are below the critical micelle concentration, the formation of positively charged complex ions is indicated.

This interpretation is in accord with the conclusion of Hiskey and Downey (1954).

Cochin and Woods (1951) gave an estimation of tetraethylammonium ions in plasma levels and urinary excretion after an intravenous injection of 20 mg/Kg of the compound. An equal amount of plasma, urine, or aqueous solution was shaken with 10% trichloroacetic acid and centrifuged. The supernatant was filtered and the filtrate shaken with aqueous bromocresol purple reagent. The indicator is 100 fold in excess of the quaternary ammonium salt. After centrifugation the chloroform extract containing indicator-quaternary ammonium complex was shaken with 0.1 N NaOH. Spectra of the alkaline layer was read in the Beckman DU Spectrophotometer at 959 mu. A straight line relationship in optical density existed between 5.0 to 35.0 micrograms/ml of
tetraethylammonium ions. Practically all of the administered drug appeared in the catheterized urine during the first six to eight hours.

Other than losses due to adsorption, another factor which is worth attention is the rate of fading of the indicator. Phenolphthalein and some of the substituted phenolphthaleins show a pronounced tendency to fade, particularly in alkaline solution. It was found that the stability could be increased by replacement of the carboxyl group in the phenolphthalein with the sulfonic acid group to form phenolsulfonphthaleins which is useful for the entire pH range for colorimetric and spectrophotometric. Generally, the extent of fading depends on the alkali concentration and length of time. The mechanism of the fading reaction has been established by Amis and LaMer (1941) in a study of the Bronsted primary salt effect. The dinegative alkaline form of the indicator \( \text{R}^{-2} \), combines with a hydroxyl ion to form the colorless carbinol \( \text{ROH}^{-3} \). Since the reaction is reversible, bimolecular constants are used to represent the fading and color-regenerating reactions.

Sager (1947) studied phenolsulfonphthalein and nine of its derivatives which have various substituents in the two chromophoric rings. All fading reactions were conducted in relatively strong alkali, 1.12 N for convenience in following the fading. The absorption of light at the maximum was observed at various time intervals. A measurable equilibrium between colored
and colorless forms was reached in a majority of cases but some fadings continued to zero absorbance. She obtained the forward and reverse rate constants and the equilibrium constant by plotting the optical density as a function of time. For complete fading a simplified equation was established. The plots are linear over the entire range of fading.

In addition to reversible fading, phenolphthaleins undergo gradual irreversible decomposition which has been attributed to oxidation by the air, but no evidence of this effect has been found for any of the sulfonphthaleins. The electronegativity of the substituents (inductive effect) and the position or site of substitution (steric effect) determine the rate of reaction with the negative hydroxyl ion in alkaline solution. More electronegative halogen as substituent makes the effective charge on the reactive central carbon atom more positive, and thus increases its rate of reaction with the negative hydroxyl ion. Substitution of a methyl or other alkyl group leads to a decrease in the rate due to an opposite inductive effect. Steric effects associated with the proximity of the substituent to reacting center of the molecule also play a similar role. Therefore both time and pH must be controlled in measuring these spectra.

Popov and Humphrey (1959) concluded that the formation of ion-pair complexes (tetraphenylarsonium salts) did not affect
the absorption spectra of the component ions. Analysis of their data, however, reveals that the maximum spectral changes are associated with the maximum changes in the amount of ion-pair complex present.
CHAPTER II

EXPERIMENTAL

I. REAGENTS

Water: The water used to prepare all solutions in the experiments was redistilled in an all pyrex still.

Matheson Scientific Co.

Brom cresol green: Tetrabromo-m-cresol-sulfonphthalein, National Aniline Division, Cat. No. 330, Lot 16937, three times recrystallized from chloroform and carbon tetrachloride, dried with vacuum pump prior to use.

l-Butanol: Analytical reagent, Cat. No. 3000, Mallinckrodt Chemical Works.

Carbon tetrachloride: Analytical reagent, Cat. No. 4368, Mallinckrodt Chemical Works.

Chloroform: Analytical reagent, Cat No. 4440, Mallinckrodt Chemical Works.

Ethanol: 95% alcohol, U.S. Industrial Chemical Co.

Ethyl acetate: Ethyl acetate anhydrous, 99.5%, Cat. No. 5212, Matheson Coleman & Bell.
Hydrochloric acid: 'Baker Analyzed' reagent, Cat. No. 9535, LOT 37423, J.T. Baker Chemical Co.
Sodium bromide: Granular, Cat. No. 0535, Mallinckrodt Chemical Works.
Sodium phosphate: 'Baker Analyzed' reagent, dibasic anhydrous, powder, Cat. No. 3828, LOT 27210, J.T. Baker Chemical Co.
Tetra-n-butylammonium bromide: Eastman organic chemicals, Cat. No. 7377. Division of Eastman Kodak Co. Recrystallized three times from ethyl acetate. Dried in vacuo.

II. PREPARATION OF SOLUTIONS FOR SPECTRA

All aqueous components added to these flasks were maintained at 25 °C in constant temperature bath before pipetting, especially tetra-n-butylammonium bromide which has a great expansion coefficient. Comparisons of experimental data at equal ionic strength are desirable. These were achieved by varying the amount of sodium bromide added with respect to the concentration of the quaternary ammonium bromide. In order to make acceptable comparisons possible, the solutions were prepared from identical portions of stock solution of indicator with the same pipette into 25 ml volumetric flasks. The amounts of indicator and acid or base added were maintained in a constant quantity. Measured amounts of tetra-n-butylammonium bromide and sodium bromide
solutions were added and the mixture made to volume at 25 °C. When ethanol was used, the indicator was dissolved in 95% ethanol. Five ml of this solution was added to the 25 ml flasks. When made to volume the solutions contained 19 volume percent ethanol. The absorbance of each solution was taken exactly 30 min after mixing, with the aid of the Beckman DU Spectrophotometer which has a photomultiplier attachment and temperature controlled cell compartment maintained 25 °C. Tap water was circulated through the lamp housing to prevent overheating. Tungsten lamp was used.

Absorptions were taken within the range of wavelength of 14,250 cm\(^{-1}\) (701.8 mu) to 23,000 cm\(^{-1}\) (434.8 mu) for basic solutions, and in the range of 16,750 cm\(^{-1}\) (597 mu) to 25,000 cm\(^{-1}\) (400 mu) for acid solutions. Absorbance due to media, cuvettes and other factors were corrected by appropriate blanks. pHS of solutions were measured immediately after spectra observations by means of the Beckman pH meter, model G. The theoretical pHS at which 99% of the indicator will be present as a single ionic species in acid and basic solutions are 1.7 and 7.7 respectively. The calculation was based on the value of pK\(_a\) of brom cresol green, which is 4.7, and on the assumption that no complexes were formed between any of the indicator species and positive ions other than hydrogen ions. Therefore at pHS less than 1.7 there will be less than 0.1% of the basic form of brom cresol green present in solution, while at pHS greater than 7.7 there will be
less than 0.1% of the acid form of the indicator present in solution. pH range for acid solutions is 1.3 - 1.5, for basic solutions is 8.0 - 8.3. Excessively high or low pHs were avoided in order to prevent the possibility of slow reactions with or catalysis by high concentrations of hydrogen or hydroxide ions.

TABLE I

COMPOSITION OF BASIC SOLUTIONS

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Control</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr (M)</td>
<td>1.92</td>
<td>1.12</td>
<td>1.60</td>
<td>1.76</td>
<td>1.84</td>
<td>1.87</td>
<td>1.91</td>
</tr>
<tr>
<td>Bu₄NBr (M)</td>
<td>0</td>
<td>0.80</td>
<td>0.32</td>
<td>0.16</td>
<td>0.08</td>
<td>0.048</td>
<td>0.016</td>
</tr>
</tbody>
</table>

TABLE II

COMPOSITION OF ACID SOLUTIONS

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Control</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr (M)</td>
<td>1.92</td>
<td>1.12</td>
<td>1.60</td>
<td>1.76</td>
<td>1.84</td>
</tr>
<tr>
<td>Bu₄NBr (M)</td>
<td>0</td>
<td>0.80</td>
<td>0.32</td>
<td>0.16</td>
<td>0.08</td>
</tr>
</tbody>
</table>
III. PREPARATION OF SOLUTIONS FOR CHROMATOGRAPHY

Acid solvent: The mixture contained 200 ml of n-butanol and 75 ml of 0.1 N HCl. The two phases obtained were separated. 40 ml of the lower layer was used to equilibrate the chamber, while 14 ml of the upper butanol layer was used as the travelling solvent.

Basic solvent: The mixture contained 1 part of ammonia, 9 parts of redistilled water and 10 parts of n-butanol. There were two phases of which 200 ml of the bottom layer was used for equilibration, and 14 ml of upper layer as travelling solvent.

In order to assure the purity of brom cresol green (BCG) purified by Miss Mersol, BCG-16-49, BCG-16-92 and BCG-16-64 were renumbered A, B, C respectively and submitted to descending chromatographic analysis. After spotted with an amount of 2 microliters and dried for an hour, the paper strips were equilibrated with acidic and basic solvents in separate chambers for at least eight hours at room temperature. About 14 ml of both upper layers were used as travelling solvents. The sealed chambers were allowed to stand at room temperature for about six or seven hours. When the solvent fronts were about one inch above the bottom of the strips, they were removed with the solvent front marked immediately, and dried on steel gauze under the hood. No round spots were observed but in smeared appearance after investigation under UV-light. Therefore three Rf values were taken for each strips, namely top, middle and bottom section of
the spot with respect to the solvent front.

IV. PURIFICATION OF BROM CRESOL GREEN AND TETRA-n-BUTYLAMMONIUM SALT

**Brom cresol green:** Ten grams of crude brom cresol green was dissolved in 340 ml of chloroform under reflux for 30 min at 80 °C. The indicator started to dissolve at 70 °C. After the solution was complete, the liquid was filtered through a fritted glass filter. 193 ml of carbon tetrachloride was added to the filtrate and seeded with BCG-1692-C (from Miss Mersol's purification), no turbidity occurred immediately. After standing for a week, the pale yellowish crystals were filtered through glass funnel. Only four grams was recovered, which was recrystallized twice, with a crop of 4 grams (wet) after long standing of two weeks. After one week, the pale yellow crystals were removed by filtration on sintered glass. An additional 2-3 grams was recovered from the mother liquors. The crystals were dried under high vacuum at room temperature.

**Tetra-n-butylammonium bromide:** The commercial material was recrystallized three times as follows:

1. 150 gm of Bu₄NBr was dissolved in 1500 ml of ethyl acetate. Solute starts to dissolve at 58-60 °C.
2. Reflux for 60 min at 80 °C.
(3) Filtered the solution through filter paper cone at 80 °C.
(4) The filtrate was left to cool to room temperature and seeded.
(5) Crystals were filtered in large glass funnel and the wet crop weighed.
(6) Recrystallization using process from (1) to (4).
(7) Dry under high vacuum at room temperature.
CHAPTER III

RESULTS

A definite change in color and in spectra has been observed between the control solutions and the solutions containing tetra-n-butylammonium bromide. The effects were obviously greater than those observed by Miss Mersol but the general effects on the spectra look like that obtained by Miss Mersol as shown in Figure 1.

At pHs greater than 8, the control solution that containing NaBr but no quaternary ammonium ions appeared to be purplish blue, while the one containing the highest concentration of tetra-n-butylammonium ions looked greenish blue. At pHs less than 1.5 the control solution appeared to be orange, while the one with the most tetra-n-butylammonium ions was pale yellowish in color. The color changes, though small, were due to the presence of quaternary ammonium ions.

The measured pHs of the basic solutions ranged from pH 8.0 to pH 8.3. The lowest energy maxima in absorption occurred at 16,250 cm⁻¹ (615.4 mu) in control solutions. With addition of tetra-n-butylammonium ion, the maximum was shifted toward lower frequency by approximately an interval of 250 cm⁻¹. This is similar to the bathochromic, hyperchromic change observed by Mersol with tetraethylammonium ion and with tetramethylammonium ion.
THE EFFECT OF TETRAALKYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY SOLUTIONS OF BROM CRESOL GREEN

Solid lines represent absorbance in 0.80 Molar Et₄NBr minus that in 0.80 Molar NaBr. Arrows indicate the position of maximum absorbance in 0.80 Molar NaBr. Dotted lines indicate measurements in 0.80 Molar Me₄NBr minus those in 0.80 Molar NaBr. (Mersol 1961)
The greatest difference in optical densities between the control solution and solution with addition of tetra-n-butylammonium ion occurred in all solutions at 15,500 cm\(^{-1}\) (645.2 μm) and at 15,250 cm\(^{-1}\). The observed values are shown in Table III. A plot

**Table III**

THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY SOLUTIONS OF BROM CRESOL GREEN

<table>
<thead>
<tr>
<th>Concentration of Bu(_4)NBr, Molar</th>
<th>Acid Solution 20,750 cm(^{-1})</th>
<th>Basic Solution 15,500 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_0 - D)</td>
<td>(D - D_0)</td>
</tr>
<tr>
<td>0.80</td>
<td>0.121</td>
<td>0.228</td>
</tr>
<tr>
<td>0.32</td>
<td>0.079</td>
<td>0.204</td>
</tr>
<tr>
<td>0.16</td>
<td>0.051</td>
<td>0.163</td>
</tr>
<tr>
<td>0.08</td>
<td>0.030</td>
<td>0.101</td>
</tr>
<tr>
<td>0.048</td>
<td>---</td>
<td>0.073</td>
</tr>
<tr>
<td>0.016</td>
<td>---</td>
<td>0.023</td>
</tr>
</tbody>
</table>

\(D_0\) is the optical density (absorbance) of the solution containing only sodium bromide. \(D\) is the absorbance of solutions in which Bu\(_4\)NBr has been substituted for part of the NaBr. Acid solutions contained 0.02 M HCl, 19 volume percent ethanol, 3.06 \(\times 10^{-5}\) M brom cresol green, and 1.12 to 1.92 M NaBr. Basic solutions contained 0.02 M Na\(_2\)HPO\(_4\), 1.26 \(\times 10^{-5}\) M brom cresol green and 1.12 to 1.92 M NaBr.
of these differences in optical densities against the concentration of tetra-n-butylammonium ion at a certain frequency is shown in Figure 2. The optical density differences increase rapidly with increase in concentration and seem to approach a constant at higher concentration. The effect of quaternary ammonium ions on the spectra is proportional in some way to their concentration. There was no detectable Tyndall effect in basic solutions.

The measured pHs of acid solutions were in range of pH 1.3 to pH 1.5. The maxima in absorption occurred at 22,500 cm$^{-1}$ (444.4 mu) in control solutions. With the addition of tetra-n-butyl ammonium ions the maxima were shifted 250 cm$^{-1}$ toward higher frequency. In solutions without ethanol, turbidity was observed from 0.002 to 0.16 M. When 10 volume percent ethanol was added, there was a turbidity at 0.08 M of Bu$_4$NBr. With 19 volume percent ethanol, there was no detectable turbidity in any solutions. The largest differences between the optical density of the control solutions and those of solutions containing quaternary ammonium ions was observed at 20,750 cm$^{-1}$ and 21,000 cm$^{-1}$, see Table III. In contrast to the bathochromic, hyperchromic shift observed in basic solution, this change is hypsochromic and seems also to be hypochromic, although this latter observation is less certain. The data are plotted in Figure 3. As seen from the curve, the rate of change is not as abrupt as that in basic solution when the quaternary ammonium ion concentration is increased. It might
THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY BASIC SOLUTIONS OF BROM CRESOL GREEN

Figure 2

D is the optical density at 15,250 cm\(^{-1}\) of a 0.0126 mMolar solution of brom cresol green in 0.020 M \(\text{Na}_2\text{HPO}_4\) and 1.92 Molar salt consisting of \(C_Q^0\) Molar \(\text{Bu}_4\text{NBr}\) and \((1.92 - C_Q^0)\) Molar NaBr. (1 cm cell)
THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY ACID SOLUTIONS OF BROM CRESOL GREEN

Figure 3

D is the optical density at 20,750 cm⁻¹ of a 0.0306 mMolar solution of brom cresol green in 19 volume percent aqueous ethanol containing 0.024 M HCl, 1.92 Molar salt consisting of \( C_Q^o \) Molar Bu₄NBr and \( (1.92 - C_Q^o) \) Molar NaBr. (1 cm cell)
approach a constant at some very high concentration of
tetra-n-butylammonium ions.

Figures 4 and 5 show the changes in absorbance of brom
cresol green caused by the substitution of Bu₄NBr for NaBr. It
should be noted that the direction of change in acid solution
(D₀ - D) is different from that observed in basic solution
(D - D₀). On these graphs and elsewhere D₀ is defined as the
absorbance at a given wavelength in the presence of 1.92 M NaBr
with no Bu₄NBr present. D is the absorbance of solution containing
identical amounts of everything except NaBr with Bu₄NBr substituted
for the missing NaBr.
THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY BASIC SOLUTIONS OF BROM CRESOL GREEN

Figure 4

$A_M \times 10^{-3}$

$\Delta A_M \times 10^{-3}$

FREQUENCY CM$^{-1}$

15,000 17,000 19,000 21,000

$A_M$ is the absorbance of brom cresol green in solutions containing $\text{Bu}_4\text{NBr}$ minus that in solutions with $\text{NaBr}$ replacing $\text{Bu}_4\text{NBr}$. Total salt 1.92 M, $\text{Na}_2\text{HPO}_4$, 0.020 M. Solution 1 is 0.80 M $\text{Bu}_4\text{NBr}$; 2 is 0.16 M; 3 is 0.048 M.
THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION ON THE ABSORPTION OF LIGHT BY ACID SOLUTIONS OF BROM CRESOL GREEN

\[ D_0 - D \]

\[ \text{FREQUENCY CM}^{-1} \]

Figure 5

\( D_0 \) is the optical density of a 0.0306 mMolar solution of brom cresol green in aqueous 19 volume percent ethanol containing NaBr minus that in otherwise identical solutions with Bu4NBr replacing some of the NaBr. Total salt was 1.92 M, HCl was 0.024 M. (1 cm cell)
## TABLE IV

THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY DINEGATIVE ION OF BROM CRESOL GREEN

At $v = 15,250$ cm$^{-1}$

<table>
<thead>
<tr>
<th>$C^0_Q$ (M)</th>
<th>$\frac{1}{C^0_Q}$ (M$^{-1}$)</th>
<th>D - $D_0$</th>
<th>$\frac{1}{D - D_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.221</td>
<td>4.52</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.196</td>
<td>5.10</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.157</td>
<td>6.37</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.097</td>
<td>10.31</td>
</tr>
<tr>
<td>0.048</td>
<td>20.83</td>
<td>0.066</td>
<td>15.15</td>
</tr>
<tr>
<td>0.016</td>
<td>62.50</td>
<td>0.024</td>
<td>41.67</td>
</tr>
</tbody>
</table>

At $v = 15,500$ cm$^{-1}$

<table>
<thead>
<tr>
<th>$C^0_Q$ (M)</th>
<th>$\frac{1}{C^0_Q}$ (M$^{-1}$)</th>
<th>D - $D_0$</th>
<th>$\frac{1}{D - D_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.228</td>
<td>4.35</td>
</tr>
<tr>
<td>0.32</td>
<td>3.15</td>
<td>0.204</td>
<td>4.90</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.163</td>
<td>6.13</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.101</td>
<td>9.90</td>
</tr>
<tr>
<td>0.048</td>
<td>20.83</td>
<td>0.073</td>
<td>13.70</td>
</tr>
<tr>
<td>0.016</td>
<td>62.50</td>
<td>0.023</td>
<td>43.48</td>
</tr>
</tbody>
</table>

$D_0$ = absorbance of brom cresol green in solution containing 1.92 M of sodium bromide.

D = absorbance of brom cresol green in solution containing $C^0_Q$ M $\text{Bu}_4\text{NBr}$ and (1.92 - $C^0_Q$) Molar sodium bromide.

Brom cresol green was $1.26 \times 10^{-5}$ M, $\text{Na}_2\text{HPO}_4$ was 0.02 M.
TABLE V

THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY DINEGATIVE ION OF BROM CRESOL GREEN*

At $v = 15,250$ cm$^{-1}$

<table>
<thead>
<tr>
<th>$C_Q$ (M)</th>
<th>$\frac{1}{C_Q}$ (M$^{-1}$)</th>
<th>$D - D_0$</th>
<th>$\frac{1}{D - D_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.211</td>
<td>4.74</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.188</td>
<td>5.32</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.139</td>
<td>7.19</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.078</td>
<td>12.83</td>
</tr>
<tr>
<td>0.048</td>
<td>20.83</td>
<td>0.053</td>
<td>18.87</td>
</tr>
<tr>
<td>0.016</td>
<td>62.50</td>
<td>0.010</td>
<td>100.00</td>
</tr>
</tbody>
</table>

At $v = 15,500$ cm$^{-1}$

<table>
<thead>
<tr>
<th>$C_Q$ (M)</th>
<th>$\frac{1}{C_Q}$ (M$^{-1}$)</th>
<th>$D - D_0$</th>
<th>$\frac{1}{D - D_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.225</td>
<td>4.44</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.194</td>
<td>5.15</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.150</td>
<td>6.67</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.090</td>
<td>11.11</td>
</tr>
<tr>
<td>0.048</td>
<td>20.83</td>
<td>0.062</td>
<td>16.13</td>
</tr>
<tr>
<td>0.016</td>
<td>62.50</td>
<td>0.008</td>
<td>125.00</td>
</tr>
</tbody>
</table>

$D_0$ = absorbance of brom cresol green in solution containing 1.92 M of sodium bromide.

$D$ = absorbance of brom cresol green in solution containing $C_Q$ M $Bu_4NBr$ and $(1.92 - C_Q)$ Molar sodium bromide.

Brom cresol green was $1.38 \times 10^{-5}$ M, $Na_2HPO_4$ was 0.02 M.

*Re-run of spectra with indicator purified by author.
TABLE VI

THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION UPON THE ABSORPTION OF LIGHT BY MONONEGATIVE ION OF BROM CRESOL GREEN

At \( v = 20,750 \text{ cm}^{-1} \)

<table>
<thead>
<tr>
<th>( C_Q^0 ) (M)</th>
<th>( \frac{1}{C_Q^0} ) (M(^{-1}))</th>
<th>( D_0 - D )</th>
<th>( \frac{1}{D_0 - D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.121</td>
<td>8.26</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.079</td>
<td>12.66</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.051</td>
<td>19.61</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.030</td>
<td>35.33</td>
</tr>
</tbody>
</table>

At \( v = 21,000 \text{ cm}^{-1} \)

<table>
<thead>
<tr>
<th>( C_Q^0 ) (M)</th>
<th>( \frac{1}{C_Q^0} ) (M(^{-1}))</th>
<th>( D_0 - D )</th>
<th>( \frac{1}{D_0 - D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.120</td>
<td>8.33</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.078</td>
<td>12.82</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.049</td>
<td>20.41</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>0.027</td>
<td>37.04</td>
</tr>
</tbody>
</table>

\( D_0 \) = absorbance of brom cresol green in solution containing 1.92M of sodium bromide.

\( D \) = absorbance of brom cresol green in solution containing \( C_Q^0 \) M \( \text{Bu}_4\text{NBr} \) and \((1.92 - C_Q^0)\) Molar sodium bromide.

Brom cresol green was \( 3.06 \times 10^{-5} \) M, HCl was 0.02 M, ethanol was 19 volume percent.
TABLE VII

THE EFFECT OF TETRA-n-BUTYLAMMONIUM ION UPON THE ABSORPTION
OF LIGHT BY MONONEGATIVE ION OF BROM CRESOL GREEN

At $v = 20,750 \text{ cm}^{-1}$

<table>
<thead>
<tr>
<th>$C^0_Q$ (M)</th>
<th>$\frac{1}{C^0_Q}$ (M$^{-1}$)</th>
<th>$D_0 - D$</th>
<th>$\frac{1}{D_0 - D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.137</td>
<td>7.30</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.091</td>
<td>10.99</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.063</td>
<td>15.87</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.04</td>
<td>25.00</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

At $v = 21,000 \text{ cm}^{-1}$

<table>
<thead>
<tr>
<th>$C^0_Q$ (M)</th>
<th>$\frac{1}{C^0_Q}$ (M$^{-1}$)</th>
<th>$D_0 - D$</th>
<th>$\frac{1}{D_0 - D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.25</td>
<td>0.134</td>
<td>7.46</td>
</tr>
<tr>
<td>0.32</td>
<td>3.13</td>
<td>0.088</td>
<td>11.36</td>
</tr>
<tr>
<td>0.16</td>
<td>6.25</td>
<td>0.064</td>
<td>15.63</td>
</tr>
<tr>
<td>0.08</td>
<td>12.25</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.04</td>
<td>25.00</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$D_0 =$ absorbance of brom cresol green in solution containing

1.92 M of sodium bromide.

$D =$ absorbance of brom cresol green in solution containing $C^0_Q$ M

$Bu_4NBr$ and $(1.92 - C^0_Q)$ Molar sodium bromide.

Brom cresol green was $3.06 \times 10^{-5}$ M, HCl was 0.02 M, ethanol
was 10 volume percent.

(---) indicates Tyndall effect.
### TABLE VIII

**DENSITIES OF BASIC AND ACID SOLUTIONS**

<table>
<thead>
<tr>
<th>Basic solutions</th>
<th>Density gm/ml</th>
<th>Calculated wt. of other species gm/25 ml</th>
<th>Calculated water gm/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1.147</td>
<td>5.015</td>
<td>946</td>
</tr>
<tr>
<td>0.80 M Bu₄NBr</td>
<td>1.097</td>
<td>9.401</td>
<td>720</td>
</tr>
<tr>
<td>Acid solutions*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>1.116</td>
<td>8.814</td>
<td>763</td>
</tr>
<tr>
<td>0.80 M Bu₄NBr</td>
<td>1.068</td>
<td>13.200</td>
<td>540</td>
</tr>
</tbody>
</table>

* with 19 volume percent ethanol

The densities of the control solutions are smaller than the one containing most quaternary ammonium ions due to the displacement of space by the very large molecules of the ions added, as can be seen from Table VIII that less amount of water is added in both basic and acid solutions. In this case the ionic strength of the solutions is hard to be maintained constant. Some suggestion of addition of an equivalent amount of glycerol or of compounds of close molecular weight is helpful.
In order to determine the nature of the interaction between the molecules of the indicator and tetra-n-butylammonium ion, the data were handled as follows:

Let $Q =$ molecule of tetra-n-butylammonium ion

$I =$ molecule of brom cresol green ion

$QI =$ molecule of complex

$C_Q^0 =$ initial concentration of a molecular species in solution

$C_I =$ final concentration of a molecular species in solution

$K' =$ apparent equilibrium constant, valid for a particular ionic strength

If one assumes a one-to-one interaction of $Q$ and $I$,

1. $Q + I = QI$

2. $K' = \frac{C_{QI}}{C_Q \times C_I}$

Since $C_Q^0$ is very much greater than $C_I^0$, one can assume $C_Q^0 = C_Q$

3. $K' = \frac{C_{QI}}{C_Q^0 \times C_I}$

But $C_{QI} = C_I^0 - C_I$

4. $K' = \frac{C_I^0 - C_I}{C_Q^0 \times C_I}$

Or

5. $K'C_Q^0 = \frac{C_I^0}{C_I} - 1$

6. $C_I = \frac{C_I^0}{(1 + KC_Q)}$
Let $D_0 = a_I C_I^0$ (control solution)

$D = a_I C_I + a_QI C_QI$

$a_x = \text{molar absorbance of } x$

7a $D - D_0 = a_I C_I + a_QI C_QI - a_I C_I^0$

7b $= a_I C_I + a_QI (C_I^0 - C_I) - a_I C_I^0$

7c $= a_I (C_I - C_I^0) + a_QI (C_I^0 - C_I)$

7d $= a_I (C_I - C_I^0) - a_QI (C_I - C_I^0)$

7e $= (a_I - a_QI) (C_I - C_I^0)$

By substituting $C_I$ from equation 6

8a $D - D_0 = (a_I - a_QI) (\frac{C_I^0}{1 + K'C_Q} - C_I^0)$

8b $= (a_I - a_QI) C_I^0 (\frac{-K'C_Q^0}{1 + K'C_Q^0})$

8c $= (a_QI - a_I) C_I^0 (\frac{K'C_Q^0}{1 + K'C_Q^0})$

by taking reciprocal of equation 8c

9a $\frac{1}{D - D_0} = \frac{1}{(a_QI - a_I) C_I^0 (\frac{1}{K'C_Q^0})}$

9b $= \frac{1}{(a_QI - a_I) C_I^0 (\frac{1}{K'C_Q^0}) + 1}$

9c $= \frac{1}{(a_QI - a_I) C_I^0} + \frac{1}{(a_QI - a_I) C_I^0 (\frac{1}{K'C_Q^0})}$

In equation 9c, $C_Q^0$ is the only variable, all others are constant.
Since $1/C_Q^0$ is the only variable on the right side of the equation, a plot of $1/C_Q^0$ versus $1/(D - D_0)$ will be linear if the assumption of equation 1 is valid. Such a plot for measurements in basic solutions (Table IV) is shown in Figure 6. The relationship is clearly linear at low concentrations $Q$, but not at high concentrations. Equation 9c can be rewritten,

$$9d \quad \frac{1}{D_0 - D} = \frac{1}{(a_I - a_{QI})C_I^0} + \frac{1}{(a_I - a_{QI})C_I^0}(\frac{1}{K' C_Q^0})$$

Again if the assumption of equation 1 is valid a plot of $1/C_Q^0$ versus $1/(D_0 - D)$ will be linear. Figure 7 shows a plot of the data obtained in acid solutions (Table VI). The relationship is clearly linear.

A somewhat different treatment of the data is that used by McConnell and Davidson (1950) for evaluation of the formation constant of CuCl$^+$. Using the same definitions and assumptions as in the previous treatment, the form of equation used by those authors is obtained by multiplying both sides of equation 9 by $C_I^0 \times C_Q^0$:

$$10 \quad \frac{C_I^0 \times C_Q^0}{D - D_0} = \frac{C_Q^0}{(a_{QI} - a_I)} + \frac{1}{K'(a_{QI} - a_I)}$$

This equation indicates that a straight line with slope $1/(a_{QI} - a_I)$ and intercept $1/K'(a_{QI} - a_I)$ would be obtained by plotting $(C_I^0 \times C_Q^0)/(D - D_0)$ versus $C_Q^0$, in the region in which only a one-to-one complex is formed between $Q$ and $I$. 
DETERMINATION OF EQUILIBRIUM CONSTANT
OF THE 1:1 COMPLEX BETWEEN
TETRA-n-BUTYLAMMONIUM ION AND
AN ION OF BROM CRESOL GREEN

$\frac{1}{(D-D_0)}$ vs $\frac{1}{C_Q}$

Figure 6

$D$ is the optical density of 0.013 Molar solution of brom cresol green in basic solution containing $C_Q^0$ Molar $Bu_4NBr$. $D_0$ is the same measurement in otherwise identical solutions with NaBr substituted for the $Bu_4NBr$. 
DETERMINATION OF EQUILIBRIUM CONSTANT
OF THE 1:1 COMPLEX BETWEEN
TETRA-n-BUTYLAMMONIUM ION AND
AN ION OF BROM CRESOL GREEN

\[ \frac{1}{(D_0 - D)} \]

\[ \frac{1}{C_Q^0} \text{ M}^{-1} \]

Figure 7

D is the optical density of a 0.031 Molar solution of brom cresol green in acid solutions containing \( C_Q^0 \) Molar Bu\(_4\)NBr. \( D_0 \) is the same measurement in otherwise identical solutions with NaBr substituted for the Bu\(_4\)NBr.
Figure 8 shows such graphs for measurements in both acidic and basic solutions. In acid solution, the quantities plotted show a linear relationship, while in basic solution the linear relationship holds in solutions below 0.2 M quaternary ammonium compound, with a clear deviation above 0.3 Molar. The values for $K'$ calculated from the graphs shown in Figure 6, 7, and 8 are collected in Table IX.

**TABLE IX**

FORMATION CONSTANTS FOR THE COMPLEX BETWEEN TETRA-n-BUTYLAMMONIUM IONS AND THE IONS OF BROM CRESOL GREEN

<table>
<thead>
<tr>
<th></th>
<th>Basic Solutions</th>
<th>Acid Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15,250 cm$^{-1}$</td>
<td>20,750 cm$^{-1}$</td>
</tr>
<tr>
<td>$K'$ from Eq. 9 plots</td>
<td>4.0 (l/m)</td>
<td>2.5 (l/m)</td>
</tr>
<tr>
<td>$K'$ from Eq. 10 plots</td>
<td>3.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Calculations at other frequencies gave 3.8, 4.0 in basic solutions 2.2, 2.2 in acid solutions.

From Figures 7 and 8 it is quite obvious that a linear relation exists between the variables plotted. This is consistent with the assumption that only one quaternary ammonium ion interacted with each brom cresol green ion. However, in basic solution Figures 6 and 8 agree that this one-to-one interaction, existing in dilute solutions of tetra-n-butylammonium ion, is not found in more concentrated solutions. The situation may be examined mathematically:
DETERMINATION OF EQUILIBRIUM CONSTANT
OF THE 1:1 COMPLEX BETWEEN
TETRA-n-BUTYLAMMONIUM ION AND
THE IONS OF BROM CRESOL GREEN

Figure 8

\[ C_Q^0 = a = \text{the molar concentration of } Bu_4\text{NBr in aqueous salt solutions of brom cresol green.} \]
\[ b = \text{the concentration of brom cresol green (0.013 mM in basic solutions, 0.031 mM in acid solutions).} \]
\[ D = \text{the optical density of solutions containing a molar } Bu_4\text{NBr,} \ D_0 = \text{that of otherwise identical solutions containing no } Bu_4\text{NBr.} \]
For situations in which additional amounts of \( Q \) react

\[ Q_I + Q = Q_2 I \]

\[ K'_2 = \frac{C_{Q_2 I}}{C_Q C_Q I} \]

\[ Q_n I + Q = Q_{n+1} I \]

\[ K'_{n+1} = \frac{C_{Q_{n+1} I}}{C_Q C_{Q_n} I} \]

Consider the absorption of light by such a solution

\[ D = a_I C_I + a_{Q_I} C_Q I + a_{Q_2 I} C_{Q_2 I} + \cdots + a_{Q_{n+1} I} C_{Q_{n+1} I} \]

This complex function could be much simplified if

\[ a_{Q_I} = a_{Q_2 I} = \cdots = a_{Q_{n+1} I} \]

\[ D = a_I C_I + a_{Q_I} \left( \sum_{j=1}^{j=n+1} C_{Q_j I} \right) \]

and since

\[ C^0_I = C_I + \left( \sum_{j=1}^{j=n+1} C_{Q_j I} \right) \]

\[ D = a_I C_I + a_{Q_I} (C^0_I - C_I) \]

From this the relationships of equation 9 would follow directly.

However, if this oversimplification is not valid, more complex relationships exist.

For \( n+1 = 2 \)

\[ D - D_o = a_I C_I + a_{Q_I} C_Q I + a_{Q_2 I} C_{Q_2 I} - a_I C^0_I \]
Since

\[ C_I^0 = C_I + C_{QI} + C_{Q2I} \]

16. \[ D - D_0 = a_IC_I + a_{QI}(C_I^0 - C_{Q2I} - C_I) + a_{Q2I}C_{Q2I} - a_IC_I^0 \]

17. \[ D - D_0 = (a_{QI} - a_I)(C_I^0 - C_I) + C_{Q2I}(a_{Q2I} - a_{QI}) \]

Equation 17 permits qualitative predictions of phenomena which may be observed if additional complexes form. In situations in which either \( C_{Q2I} \) or \( (a_{Q2I} - a_{QI}) \) are small, the first term of equation 17 will govern, and the relationships of equations 9 and 10 will be found, with linear plots of appropriate quantities as already discussed. However, when the second term is appreciable, deviations from the relationships indicated by equations 9 and 10 are expected. Such deviations are found in basic solutions (Figures 6 and 8), but not in acid solutions (Figures 7 and 8). Since equations 9 and 10 were derived from an expression identical with equation 17 minus the last term, it was convenient to examine the values of \( \Delta D \) as a function of \( C_Q \) calculated from the values of \( K' \) and \( (a_{QI} - a_I) \) given in Table IX. In acid solutions the calculated values agree very well with the experimental values, indicating that a one-to-one interaction of tetra-n-butylammonium ion and the mononegative ions of brom cresol green accounts for the color change observed in these solutions.

This is not the case in basic solutions. Here the calculated values of \( \Delta D \) agree well with the experimental values.
at low concentrations of tetra-n-butylammonium bromide, but are much larger than the experimental values at higher concentrations (0.3 - 0.8 M) of Bu₄N⁺. This indicates that for the dinegative ion of brom cresol green, the term \((a_{Q2I} - a_{QI})\) is negative which, in turn, means that the interaction of the second "Q" with the indicator part of the complex QI is in some way different than the interaction of the first "Q" with the indicator.

Mersol has shown (1961) that the absorption of light by the mono- and di-negative ions of brom cresol green is not changed by adding up to 0.8 Molar sodium bromide to the buffered solutions of these ions. Since these spectra are changed measurably by substitution of even 0.1 Molar tetraalkylammonium ions for some of the sodium ions, it is obvious that the effective interaction of the indicator anions with tetraalkylammonium ions is in some way different than that with sodium ions.

From the nature of the cations used, the formation of covalent bonds is most unlikely, therefore the possibility of ion-pair complexes was considered. The data of Hogen-Esch and Smid (1966) indicates that the formation of "contact ion-pairs" affects the spectra of several negative ions, while the formation of "solvent separated ion-pairs" has no significant effect. On the basis of these and other considerations (Mersol, 1961), it appears that the color changes reported in this thesis are due to the formation of "contact" ion-pairs. Even though the initial effects are opposite--bathochromic with dinegative brom cresol green and
hypo­chro­mic with the mononega­tive ion, the basic cause is the same—a close inter­ac­tion of the pos­i­tively charged ion with the portion of the mole­cu­le which absorbs light, with result­ing per­tur­ba­tion of the energy lev­els. In the case of the dinega­tive ion, the pos­i­tive charge increases the deloca­li­za­tion of a nega­tive charge into the ben­zenoid rings, thus reduc­ing the inter­nal energy of the ground state. The effect is, however, even greater in the upper state, so that a batho­chro­mic effect is pre­dicted in agree­ment with expe­ri­ment. With the mononega­tive brom cresol green on the other hand, the close approach of the pos­i­tive charge reduces the amount of deloca­li­za­tion of elec­trons out of the ben­zenoid rings. Again this effect is greater in the upper state and a hypo­chro­mic effect is pre­dicted, as observed.

It is some­what harder to account for the effect of a second Bu₄N⁺ binding to the com­plex of tetra-n-bu­tyl­am­mon­ium and brom cresol green. It is pos­si­ble that this inter­ac­tion changes the shape of the mole­cu­le and limits to some extent the effect of the first inter­ac­tion. Since neither inter­ac­tion is com­plete at attainable con­cen­tra­tions of quasi­ter­na­ry ammon­ium ion, it is point­less to pur­sue this prob­lem beyond the dem­on­stra­tion that such an inter­ac­tion exists.

It should be pointed out that expe­ri­ments in aque­ous acid solu­tion gave de­finite ev­i­dence that more than one tetra-n-bu­tyl­am­mon­ium ion can inter­act with a single mononega­tive brom cresol green ion. The turbid­i­ty ob­served at 0.002 M Bu₄N⁺ cleared
up above 0.16 M. In agreement with the results of Marsol (1961) with brom cresol green and cetyltrimethylammonium ions, removal of the precipitate by centrifugation revealed the same absorption spectrum, at lower density values--indicating the removal of brom cresol green. The solution of this one-to-one compound in excess of quaternary ammonium ion gives no information about the effect of this secondary interaction of the spectra. The addition of ethanol prevented precipitation at all concentrations of Bu₄N⁺, and the information in Figures 7 and 8 indicate that there is no spectra change caused by interaction of more than one quaternary ammonium ion in the experiments reported.
The interaction of tetra-n-butylammonium ion with the mono-negative ion of brom cresol green has been shown to be a one-to-one interaction of the ions to form a "contact" ion-pair. With the di-negative ion of brom cresol green the interaction is more complex. A one-to-one "contact" ion-pair is formed in dilute solution of quaternary ion, but before the formation of this complex is completed, an additional interaction begins. The apparent contradiction between the fact that "contact" ion-pair formation results in a hypsochromic change in the absorption spectra with mono-negative brom cresol green and a bathochromic change with di-negative indicator is resolved by examining the changes in energy levels of the ions caused by close proximity to a positively charged ion.
BIBLIOGRAPHY


The thesis submitted by Daniel Yue-King Chan has been read and approved by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated, and that the thesis is now given final approval with reference to content, form and mechanical accuracy.

The thesis is therefore accepted in partial fulfillment of the requirements for the Degree of Master of Science.

May 20, 1967

Date

Signature of Adviser