

New Spectrophotometric Determination of Inorganic Bromide and Chloride Salts in Aqueous Solutions

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Abstract □ A new method for the determination of inorganic salts of chloride and bromide is described. The method is based on the facts that iodine forms complexes with the anions and that these complexes absorb strongly in the UV region. The molar absorptivities of I_2Br^- at 265 nm and I_2Cl^- at 245 nm were calculated to be 3.27×10^4 and $2.3 \times 10^4 M^{-1} cm^{-1}$, respectively.

Keyphrases □ Inorganic salts—spectrophotometric determination of aqueous solutions □ Salts—spectrophotometric determination of inorganic bromide and chloride salts in aqueous solutions □ Complexes—iodine with inorganic bromide and chloride salts, spectrophotometric determination

Various methods are available for the quantitative determination of chloride and bromide ions in aqueous solutions. Some of these methods are volumetric and gravimetric (1-4) and, therefore, are laborious, time consuming, and expensive to do routinely. Relatively newer methods (5) based on the use of ion selective electrodes are excellent. However, in view of their lack of selectivity, it is necessary to have an electrode for each ion and its reagent (6).

This report describes a sensitive and simple spectrophotometric method for the determination of these halides. The method is based on the fact that both chloride and bromide ions interact with iodine in solution to form complexes that absorb strongly in the UV region.

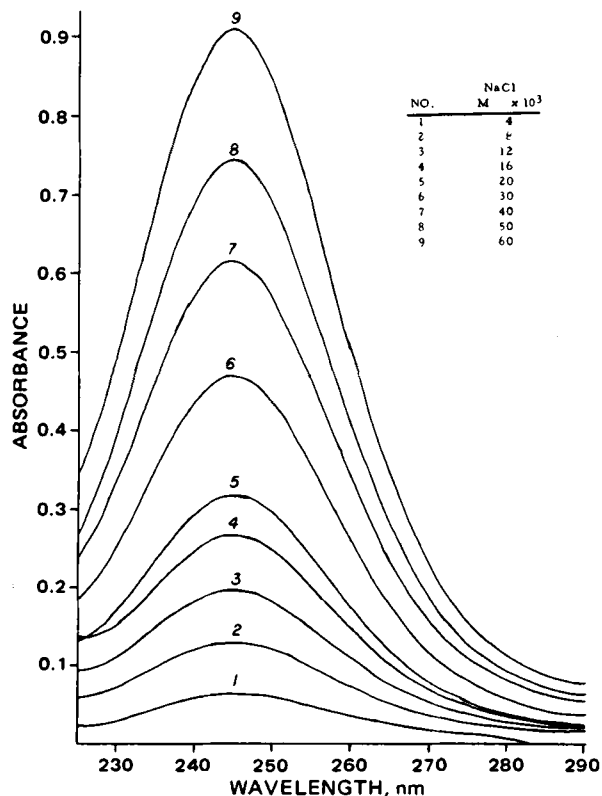
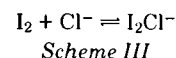
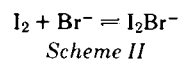
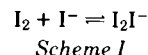


Figure 1—UV spectra of solutions containing $3 \times 10^{-4} M I_2$ and varying amounts of sodium chloride (NaCl).

BACKGROUND

Iodide, bromide, and chloride ions are known to interact with iodine in solution to form complexes of the type I_2X^- (7) (Schemes I-III).



The equilibrium constants, defined as:

$$K = \frac{(I_2X^-)_{eq}}{(I_2)_{eq}(X^-)_{eq}} \quad (Eq. 1)$$

for Schemes I-III have been reported to be 702, 11.0, and 2.1, respectively (7). These values were confirmed in this study using a different technique based on phase solubility.

Although iodide absorbs rather strongly at 238 nm and can be determined spectrophotometrically, chloride and bromide ions have no UV absorbance in this region. However, when chloride or bromide salts are added to an aqueous iodine solution to form I_2Br^- and I_2Cl^- , these solutions absorb light strongly in the UV region. The maximum absorbances for I_2Br^- and I_2Cl^- are at 265 and 245 nm, respectively, whereas iodine at the same concentration absorbs insignificantly (Figs. 1 and 2). Furthermore, the absorbance of solutions containing fixed amounts of iodine and varying amounts of the halides increases linearly as a function of the concentration of the halides (Figs. 3 and 4).

In view of this information, it would be possible to determine quantitatively both chloride and bromide in aqueous solutions.

EXPERIMENTAL

Reagents and Equipment—A saturated stock iodine solution was prepared by adding 2 liters of double-distilled water to 5 g of iodine. The solution was left overnight on a shaker to reach saturation. The saturated solubility of iodine in water at 25° was found by titration to be 7.5×10^{-4}

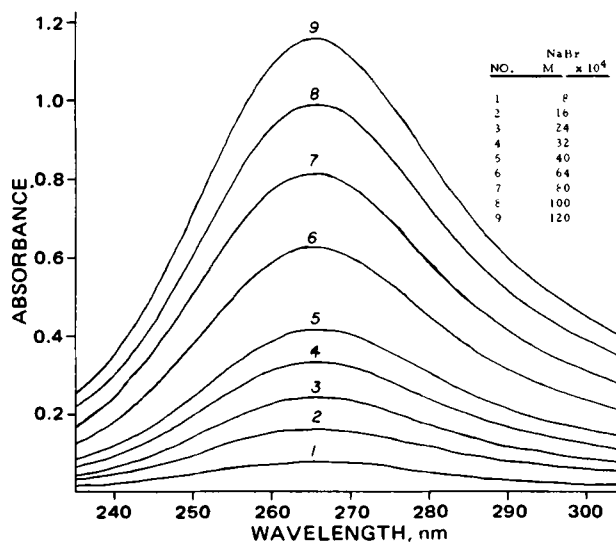


Figure 2—UV spectra of solutions containing $3 \times 10^{-4} M I_2$ and varying amounts of sodium bromide (NaBr).

Table I—Concentration of I₂Br⁻ Calculated from Eq. 1 as a Function of Added Sodium Bromide and the Corresponding UV Absorbance at 265 nm^a

Sodium Bromide Added, M × 10 ⁴	I ₂ Br ⁻ Calculated, M × 10 ⁶	UV Absorbance at 265 nm
8	2.54	0.080
16	5.08	0.160
24	7.42	0.240
32	9.81	0.530
40	12.2	0.420
64	19.0	0.620
80	23.4	0.820
100	28.6	0.990
120	33.8	1.150

^a All samples contained 3 × 10⁻⁴ M I₂.

M, in good agreement with the reported value (8). Sodium iodide, sodium chloride, and sodium bromide were analytical reagent grades.

A recording spectrophotometer¹ was used.

Phase Solubility Study—Into a 25-ml screw-capped vial with a polytetrafluoroethylene lining, 0.1 g of iodine was placed. Then 12 ml of sodium chloride or sodium bromide solution of known concentration was added. The vials were left in the shaker for 24 hr, and 10 ml of the supernatant liquid was titrated with 1 × 10⁻³ M sodium thiosulfate. The iodine concentration was calculated and plotted against the concentration of the halide added.

Spectrophotometric Analysis—To each 20 ml of the saturated iodine solution (7.5 × 10⁻⁴ M) placed in 50-ml volumetric flasks, different volumes of 0.01 M NaBr or 0.1 M NaCl were added to obtain halide concentrations ranging from 8 × 10⁻⁴ to 1.2 × 10⁻² M for sodium bromide and 4 × 10⁻³ to 6 × 10⁻² M for sodium chloride. The volumes were completed to 50 ml with double-distilled water. The UV spectra of the solutions were then measured spectrophotometrically against a blank iodine solution prepared as already described. Common impurities normally found in these salts such as phosphate, sulfate, and carbonate have no effect on the absorbance of these solutions.

Stability of Solutions—The UV spectra of the solutions were determined immediately after their preparation and 3 hr later. No change in the UV absorbance was observed.

Comparison between USP and Spectrophotometric Analyses of Sodium Chloride Tablets USP—To compare the reliability of this method for analyzing dosage forms, three tablets² were weighed indi-

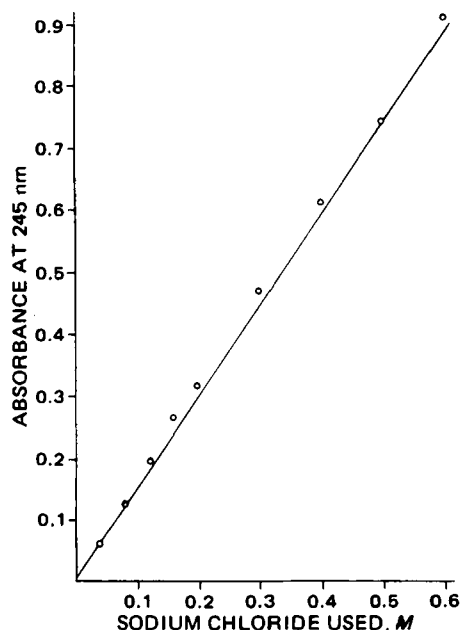


Figure 3—Plot showing a linear increase in the absorbance at 245 nm of solutions containing the same concentration of iodine, 3 × 10⁻⁴ M, and varying concentrations of sodium chloride (NaCl).

¹ Varian model 118.

² Eli Lilly lot IFB50A.

Table II—Concentration of I₂Cl⁻ Calculated from Eq. 1 as a Function of Added Sodium Chloride and the Corresponding UV Absorbance at 245 nm^a

Sodium Chloride Added, M × 10 ³	I ₂ Cl ⁻ Calculated, M × 10 ⁶	UV Absorbance at 245 nm
4	2.85	0.065
8	5.65	0.130
12	8.39	0.198
16	11.1	0.265
20	13.7	0.320
30	20.1	0.470
40	26.3	0.615
50	32.1	0.742
60	37.7	0.910

^a All samples contained 3 × 10⁻⁴ M I₂.

Table III—Results and Comparisons of the USP and Spectrophotometric Methods Using Commercial Sodium Chloride Tablets USP

Weight of Tablet, g	USP Method, g	Spectrophotometric Method, g
1.015	1.016	1.018
1.010	1.014	1.015
1.020	1.021	1.020

vidually and dissolved in 100 ml of double-distilled water. Then 25 ml of each solution was titrated according to the USP method (1). The same solutions were analyzed spectrophotometrically by pipetting 10 ml into a 50-ml volumetric flask. To this solution, 10 ml of the saturated iodine solution was added. The solutions were analyzed spectrophotometrically, and the concentration of sodium chloride was calculated by comparing the absorbance of these solutions to that of a standard sodium chloride solution treated similarly.

RESULTS AND DISCUSSION

Figure 5 shows the results of the phase solubility studies between iodine and chloride and bromide ions. The equilibrium constants determined

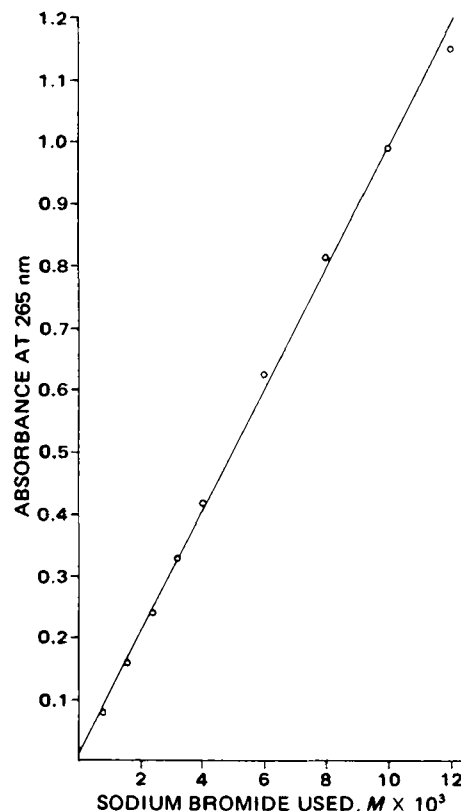


Figure 4—Plot showing a linear increase in the absorbance at 265 nm of solutions containing the same concentration of iodine, 3 × 10⁻⁴ M, and varying concentrations of sodium bromide (NaBr).

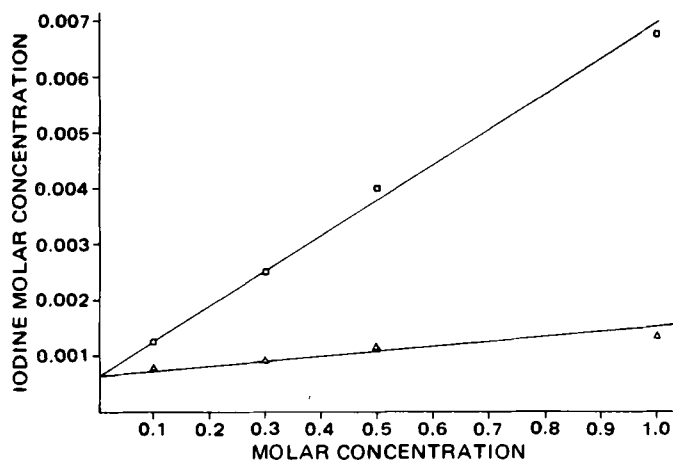


Figure 5—Plot showing the increase in the solubility of iodine as a function of added sodium chloride (Δ) and sodium bromide (\square).

from the slope of the lines of Fig. 5 were 10.6 and 2.4 for bromide and chloride, respectively, in good agreement with reported values (7).

Figures 1 and 2 show the UV absorbances of solutions containing $3 \times 10^{-4} M I_2$ and varying concentrations of sodium bromide and sodium chloride. A linear relationship between the absorbance at the corresponding wavelengths and the concentration of the added halide salts was observed. It is apparent from the data of Figs. 1 and 2 that the change

in the magnitude of the absorbance as a function of the added halide was due to changes in the concentration of the complexes formed in solution.

The concentrations of I_2Br^- and I_2Cl^- can be calculated as a function of added halides using Eq. 1 (Tables I and II). The calculated molar absorptivities were 3.27×10^4 and $2.3 \times 10^4 M^{-1} cm^{-1}$ for I_2Br^- and I_2Cl^- , respectively.

Table III shows the results obtained for the determination of sodium chloride tablets by the USP and spectrophotometric methods. The agreement between the two methods was excellent. In practice, it is advisable to determine the unknown together with a known sample using the same iodine concentration in both samples.

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Stability of 10-Acetylphenothiazine

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Received April 7, 1978, from the *Farmaceutisch Laboratorium Rijksuniversiteit Utrecht, Catharijnesingel 60, Utrecht, The Netherlands*. Accepted for publication August 30, 1978.

Abstract □ The degradation kinetics of 10-acetylphenothiazine were studied after isolation and identification of its degradation products, phenothiazine, phenothiazine-5-oxide, 3*H*-phenothiazine-3-one, and 7-(10'-phenothiazinyl)-3*H*-phenothiazine-3-one. The acetyl group was not present in any degradation product. The degradation rate was independent of oxygen but highly pH dependent, indicating a specific hydrogen-ion-catalyzed hydrolysis of 10-acetylphenothiazine to give phenothiazine, which was oxidized. The experimental values for the phenothiazine concentration were in good agreement with values calculated on the basis of this assumption, both in the presence and absence of oxygen.

Keyphrases □ 10-Acetylphenothiazine—stability and degradation kinetics, pH dependency □ Phenothiazines—10-acetylphenothiazine, stability and degradation kinetics, pH dependency □ Degradation—10-acetylphenothiazine, kinetics, effect of pH

The kinetics and mechanism of the oxidative degradation of phenothiazine and its 10-methyl derivative were described previously (1, 2). In this paper, the influence of the introduction of an acetyl group on stability is investigated. The 10-acetyl derivative can be considered as a model compound for the phenothiazines having a carbonyl function next to the nitrogen atom; these compounds possess antiarrhythmic properties (3). The electron-withdrawing properties of the acetyl group could possibly have a strong stabilizing effect on the phenothiazine ring system.

EXPERIMENTAL

Materials—10-Acetylphenothiazine¹ (I) was recrystallized from 96% ethanol, mp 204°, and had a molar absorptivity at 257 nm of 10,194. TLC of the recrystallized product in various systems showed only one spot, so no further purification was performed.

All other materials were as previously described (1).

Isolation and Identification of Degradation Products—Compound I was dissolved in 52.5% ethanol, buffered to an apparent pH of 2.8 with sodium acetate-hydrochloric acid (4), and stored in the dark at 85° for 3 days after saturation with oxygen. The degradation products were extracted with carbon tetrachloride and isolated by TLC and column chromatography. Silica gel and aluminum oxide were used as adsorbents, and the solvents were ether, petroleum ether, chloroform, acetone, and their mixtures. The best separation was obtained with aluminum oxide and ether and silica gel and chloroform, both giving five zones. When the degradation was carried out at pH 1.7, the same products were found by TLC as at pH 2.8.

To isolate the degradation products, the carbon tetrachloride extract was evaporated to dryness under reduced pressure at room temperature and the residue was dissolved in ether. This solution was put onto a silica gel column, and the column was then eluted with ether until the colored products had left the column. Because one degradation product was not eluted with ether, the elution was continued with acetone, giving a solution that contained only one degradation product.

The ether eluate was evaporated to dryness under reduced pressure at room temperature, and the residue was dissolved in ether-petroleum ether (1:3). This solution was put onto an aluminum oxide column, and

¹ 10-Acetylphenothiazine was a gift from Dr. C. D. M. ten Berge, Farmaceutisch Laboratorium, Groningen, The Netherlands.