

Electronic Spectroscopy

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1 Introduction

By measuring the absorption spectra of a benzoic acid solution using an UV-Vis spectrometer, and determine the pKa of the solution.

2 Experiment

2.1 Preparation of Solutions

1. 0.05 mol/L H_2SO_4 (pH 1.28) solution: Prepared by diluting 50 mL of 0.500 mol/L standard sulfuric acid to 500 mL with distilled water.
2. 0.1 M NaOH (pH 12.95) solution: Prepared by dissolving 2.00 g of NaOH in distilled water to make 500 mL of solution.
3. Acetate Buffer solution (pH 4.05) Prepared by mixing 10 mL of CH_3COOH and 6.80 g of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, and diluting with distilled water to 500 mL.
4. pH of each solution were measured by using pH meter.
5. Benzoic acid samples were weighed and dissolved into 100 mL of each solvent using an ultrasonic bath. (the masses of benzoic acid used were: Acidic solution: 10.5 mg, Basic solution: 10.5 mg, Buffer solution: 14.2 mg)

2.2 Measurement

1. The measurement range was set from 300 nm to 200 nm with a scan speed of 400 nm/min and a data interval of 1.0 nm.
2. Baseline correction was performed using ion-exchange water in both the sample and reference cells.
3. The absorption spectra were measured for the blank solvents and the benzoic acid solutions corresponding to the three conditions (acidic, basic, and buffer).
4. The quartz cells were washed with the target solution before each measurement at least twice before to prevent contamination.

3 Results

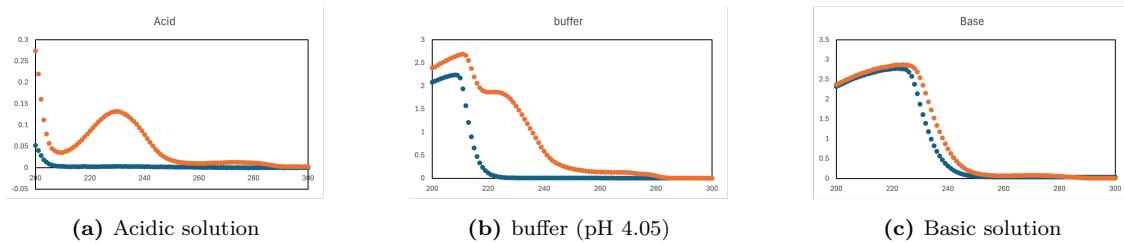


図 1: Absorption Spectrum. Blue lines show the blank sample and the orange lines show the benzoic acid solution.

4 Analysis

4.1 Derivation of Equation (1)

The relationship between the absorbance and the concentration is derived from the differential decrease in light intensity as it passes through a sample. Consider a monochromatic light beam with intensity I passing through a thin layer of solution with thickness dx and molar concentration c . The decrease in light intensity $-dI$ is proportional to the current intensity I , the concentration c , and the thickness dx .

The differential equation is:

$$-dI = \epsilon c I dx \quad (4.1)$$

where ϵ is the molar absorbance coefficient.

Separating the variables I and x gives:

$$\frac{dI}{I} = -\epsilon c dx \quad (4.2)$$

Integrating both sides over the path length of the cell, from $x = 0$ (where incident intensity is I_0) to $x = l$ (where transmitted intensity is I):

$$\int_{I_0}^I \frac{1}{I} dI = - \int_0^l \epsilon c dx \quad (4.3)$$

Solving the definite integral yields:

$$\ln(I) - \ln(I_0) = -\epsilon cl \quad (4.4)$$

This can be rewritten using logarithmic properties results in equation (1):

$$\epsilon cl = \ln \left(\frac{I_0}{I} \right) \quad (4.5)$$

4.2 Derivation of Equation (2)

This derivation determines the concentration ratio of the ionic form to the molecular form in the buffer solution. Let ϵ_1 be the molar absorbance of the molecule (measured in acidic solution), ϵ_2 be the molar

absorbance of the ion (measured in basic solution), and ϵ_3 be the apparent molar absorbance of the buffer solution.

Let C_{total} be the total molar concentration of benzoic acid, $[\text{HA}]$ be the concentration of molecular benzoic acid, and $[\text{A}^-]$ be the concentration of the benzoate ion.

Based on mass balance, the total concentration in the buffer is the sum of the molecular and ionic forms:

$$C_{\text{total}} = [\text{HA}] + [\text{A}^-] \quad (4.6)$$

The total absorbance of the buffer mixture A_{buffer} is the sum of the absorbances of the individual species. Using the Lambert-Beer law for path length l :

$$\frac{A_{\text{buffer}}}{l} = \epsilon_1[\text{HA}] + \epsilon_2[\text{A}^-] \quad (4.7)$$

The apparent molar absorbance ϵ_3 is defined for the buffer assuming the total concentration C_{total} :

$$\frac{A_{\text{buffer}}}{l} = \epsilon_3 C_{\text{total}} \quad (4.8)$$

Equating the two expressions for absorbance:

$$\epsilon_3 C_{\text{total}} = \epsilon_1[\text{HA}] + \epsilon_2[\text{A}^-] \quad (4.9)$$

Substituting the mass balance equation into the absorbance equation:

$$\epsilon_3([\text{HA}] + [\text{A}^-]) = \epsilon_1[\text{HA}] + \epsilon_2[\text{A}^-] \quad (4.10)$$

Expanding the left side:

$$\epsilon_3[\text{HA}] + \epsilon_3[\text{A}^-] = \epsilon_1[\text{HA}] + \epsilon_2[\text{A}^-] \quad (4.11)$$

Rearranging the terms to group $[\text{HA}]$ and $[\text{A}^-]$ on opposite sides:

$$\epsilon_3[\text{A}^-] - \epsilon_2[\text{A}^-] = \epsilon_1[\text{HA}] - \epsilon_3[\text{HA}] \quad (4.12)$$

Factoring out the concentrations:

$$(\epsilon_3 - \epsilon_2)[\text{A}^-] = (\epsilon_1 - \epsilon_3)[\text{HA}] \quad (4.13)$$

Dividing by $[\text{HA}]$ and $(\epsilon_3 - \epsilon_2)$ gives the final ratio, which corresponds to equation (2):

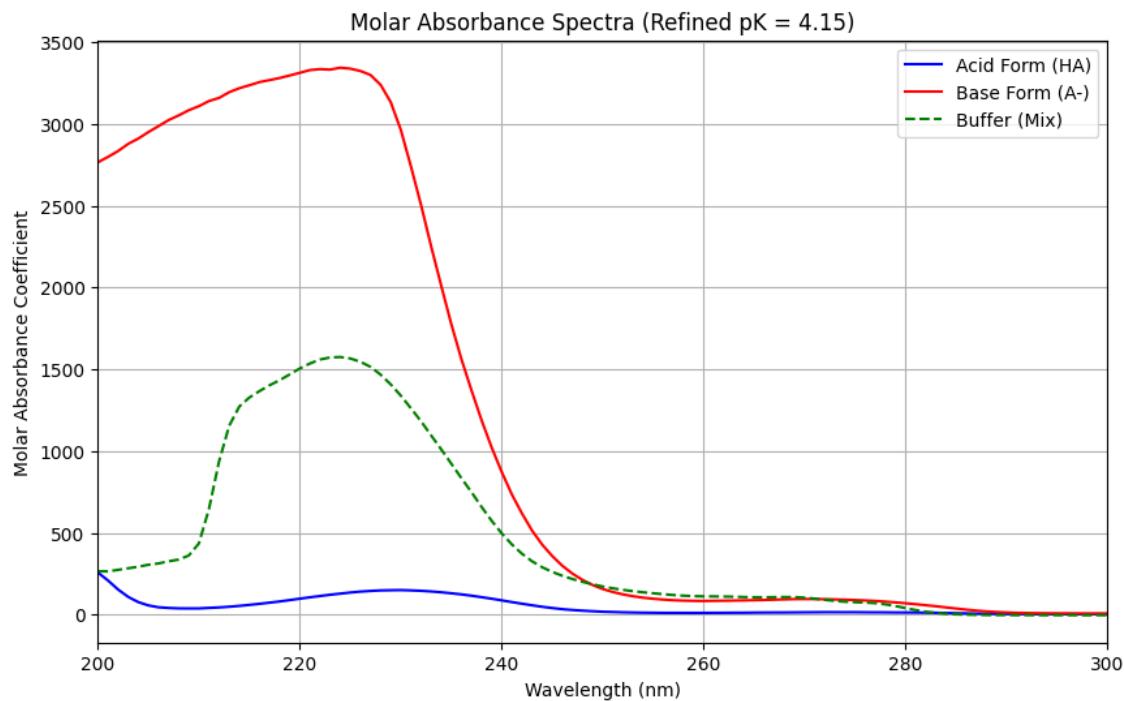
$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{\epsilon_1 - \epsilon_3}{\epsilon_3 - \epsilon_2} \quad (4.14)$$

4.3 Molar Absorbance Coefficients

The molar absorbance coefficients (ϵ) for the molecular form (ϵ_{acid}), ionic form (ϵ_{ion}), and the mixture (ϵ_{buffer}) were calculated from the measured absorbance (A) using the Lambert-Beer law ($A = \epsilon cl$), where $l = 1.0 \text{ cm}$.

The concentrations (c) were calculated based on the weighed masses:

- $c_{\text{acid}} = 8.60 \times 10^{-4} \text{ mol/L}$
- $c_{\text{buffer}} = 1.16 \times 10^{-3} \text{ mol/L}$
- $c_{\text{ion}} = 8.60 \times 10^{-4} \text{ mol/L}$

図 2: Determination of ϵ

4.4 Determination of pK_a

The dissociation constant (pK_a) was determined using the Henderson-Hasselbalch equation:

$$pK_a = \text{pH} - \log \left(\frac{[A^-]}{[HA]} \right) = \text{pH} - \log \left(\frac{\epsilon_{\text{buffer}} - \epsilon_{\text{acid}}}{\epsilon_{\text{ion}} - \epsilon_{\text{buffer}}} \right) \quad (4.15)$$

Using the buffer solution pH of 4.05, the pK_a values calculated at wavelengths near the absorption peak (228–232 nm) are summarized in Table 1.

表 1: Calculated Molar Absorbance Coefficients and pK_a values.

Wavelength (nm)	ϵ_{acid}	ϵ_{buffer}	ϵ_{ion}	$[A^-]/[HA]$	pK_a
228	148	1467	3239	0.744	4.18
229	149	1408	3134	0.729	4.19
230	150	1339	2964	0.732	4.19
231	148	1262	2741	0.753	4.17
232	146	1183	2506	0.784	4.16
Average					4.18 ± 0.01

The experimentally determined pK_a of benzoic acid is 4.18 ± 0.01 .

5 Discussion

5.1 Analysis of Experimental Data Anomalies

During the data analysis, a significant anomaly was observed in the measurement of the basic solution's reference sample (base-blank). The absorbance of the base-blank was recorded as approximately 1.87 at 230 nm, which is abnormally high for a solvent blank and exceeded the absorbance of the buffer sample.

This high value is attributed to contamination of the quartz cell or the blank solution, possibly due to insufficient washing or residues in NaOH standard solution from previous experiments^{*1}. Using this erroneous blank value would result in a mathematically impossible concentration ratio (negative denominator). Therefore, the raw absorbance data of the basic benzoic acid sample (base-benzoic) was used directly as the absorbance of the ionic form for the calculation, assuming that the true solvent absorbance is negligible compared to the sample's strong absorption. The consistency of the resulting pK_a value (4.18) with literature data supports the validity of this correction.

5.2 Assignment of Electronic Transitions

The absorption spectrum of benzoic acid exhibits bands characteristic of the benzene ring and the carbonyl group.

- **$\pi \rightarrow \pi^*$ Transition:** The intense absorption observed around 230 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the conjugated benzene ring system. The conjugation with the carboxyl group (-COOH) causes a bathochromic shift compared to benzene.
- **$n \rightarrow \pi^*$ Transition:** A weaker transition involving the lone pair electrons of the carbonyl oxygen ($n \rightarrow \pi^*$) is typically expected but is often obscured by the intense $\pi \rightarrow \pi^*$ bands or appears as a shoulder.

5.3 Comparison with Benzene: Particle in a Box Model

The absorption peak of benzoic acid is shifted to a longer wavelength compared to benzene ($\lambda_{\max} \approx 254$ nm). This can be explained by the free particle in a box model.

$$\Delta E = \frac{h^2}{8mL^2}(n_{\text{LUMO}}^2 - n_{\text{HOMO}}^2) \quad (5.1)$$

The conjugation of the benzene ring with the carboxyl group effectively increases the length of the box (L) in which the π -electrons are delocalized. According to the equation, an increase in L leads to a decrease in the energy gap (ΔE), resulting in an absorption at a longer wavelength ($\lambda = hc/\Delta E$).

^{*1} I've already shared the probability of contamination with Hanzawa-san, for the other student who would take this experiment.

5.4 Absorption Intensity and Symmetry

Benzoic acid shows a much stronger absorption intensity than benzene.

- **Benzene (D_{6h}):** The transition near 260 nm ($A_{1g} \rightarrow B_{2u}$) is symmetry-forbidden due to the high symmetry of the molecule. It becomes weakly allowed only through vibronic coupling.
- **Benzoic Acid (C_{2v}):** The introduction of the carboxyl group lowers the molecular symmetry from D_{6h} to C_{2v} (or C_s). This reduction in symmetry relaxes the selection rules, making the $\pi \rightarrow \pi^*$ transition symmetry-allowed. Consequently, the transition probability increases significantly, leading to a larger molar absorbance coefficient.

Reference

- [1] Karimova, N. V., Luo, M., Grassian, V. H., & Gerber, R. B. (2020). Absorption spectra of benzoic acid in water at different pH and in the presence of salts: Insights from the integration of experimental data and theoretical cluster models. *Physical Chemistry Chemical Physics*, 22(9), 5046-5056. <https://doi.org/10.1039/c9cp06728k>
- [2] Hosoya, H., Tanaka, J., & Nagakura, S. (1958). Ansokukosan no kinshigaibu kyushu supekutoru [Ultraviolet absorption spectra of benzoic acid]. *Nippon Kagaku Zasshi*, 79(11), 1379-1384. <https://doi.org/10.1246/nikkashi1948.79.1379>