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The Effect of pH Towards Copper (II) Bromide Reaction in Surfactant Determination

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Abstract

This study explores the interaction between copper (II) bromide ($CuBr_2$), triethylamine (TEA), and sodium dodecyl sulfate (SDS) to enhance the detection of anionic surfactants in aqueous environments. Anionic surfactants, widely present in household, agricultural, and industrial products, contribute significantly to environmental pollution due to their persistence and potential toxicity. Traditional detection methods, such as the Methylene Blue Active Substances (MBAS) technique, rely on hazardous solvents like chloroform and are labour-intensive, posing environmental and health risks. This research proposes a novel spectrophotometric approach utilizing $CuBr_2$ as an ion-pairing agent, eliminating the need for toxic solvents while improving accuracy and efficiency and focusing on determining the effect of pH on the interaction between SDS and $CuBr_2$. Solutions were prepared with varying concentrations of SDS (0.05 mM to 0.5 mM) and adjusted to pH levels of 4, 6, and 10 using hydrochloric acid and sodium hydroxide. A calibration curve was constructed at a wavelength of 650 nm to demonstrate the linear relationship between SDS concentration and absorbance, adhering to Beer-Lambert's law. The R^2 of 0.936 was obtained as well as the linear equation, $y = 0.1111x+0.0575$. Results revealed that pH significantly influences the reaction dynamics, with pH 6 identified as the optimal range for efficient ion-pairing and the formation of surfactant-metal complexes. The study provides an effective method for quantifying surfactants in synthetic water samples, enhancing environmental monitoring capabilities while minimizing chemical hazards. This research paves the way for further advancements in water quality assessment and pollutant control.

1. Introduction

Surfactants possess both hydrophobic and hydrophilic components, making them amphipathic. Surfactant originates from the term Surface Active Agents, representing a crucial group of additives in reducing surface tension. When all surfaces are saturated, surfactants begin to self-assemble in water into supramolecular aggregates. These formations in surfactants are commonly referred to as micelles, denoting assemblies beyond individual molecules, where the arrangement of the hydrophobic tails constitutes the inner core, while the hydrophilic heads are outward-facing, interacting with the surrounding aqueous environment [1]. Surfactants are widely used in various human activities due to their outstanding wetting and emulsifying properties. Anionic surfactants are the main agents that were utilized in all-purpose cleaners which will cause potential negative consequences on both biotic and abiotic components of the ecosystem [2]. However, a significant quantity of surfactant wastewater is released into the environment, leading to adverse effects on aquatic organisms, water pollution, and risks to human health. Hence, it is crucial to oversee and regulate the discharge of surfactants into environmental water. Table 1 shows the environmental risks of various surfactants. Surfactants pollute water and have an indirect impact on the environment and living things when they accumulate in bodies of water as a result of runoff from home and industrial operations.

Table 1: Environmental risks of various surfactants

Surfactants in environment	Classes of surfactant	Risks	References
Linear Alkyl Benzene Sulfonates	Anionic	Non-conservative behaviour	[3]
Perfluorinated surfactants	Anionic	Persistence, recalcitrance and toxicity	[4]
Quaternary Ammonium Ethoxylates and Cetrimonium Chloride	Cationic	Very toxic in the environment	[5]
Alkylphenol Ethoxylates	Non-ionic	Degraded and transformed products (nonyl-/octylphenol ethoxylates) are toxic as well as persistent in the environment	[6]
Alcohol Ethoxylates	Non-ionic	Highly hydrophobic and impressive adsorptive capacity on solid particles and sediments. Exposure to aquatic organisms	[4]

Consequently, surfactants are identified using many approaches in Table 2, including spectrophotometry, titration, and chromatography. Surfactant analysis can be conducted through various techniques, including spectroscopy, HPLC, and potentiometry titration. Spectroscopy utilizes light to examine how surfactants interact with electromagnetic radiation, providing insights into their chemical structure and concentration. HPLC, on the other hand, separates surfactants based on their chemical properties, allowing for precise identification and quantification. Lastly, potentiometry titration measures the potential difference in a solution during titration to determine surfactant concentration, typically by observing changes in voltage as a reagent is added, which reflects the surfactant's charge or acid-base properties. These methods are essential for analyzing and characterizing surfactants in various applications.

Table 2: Typical methods of surfactant analysis

Techniques Employed	Specific Analytes	References
Potentiometry titration	Methylene blue active substances (MBAS)	[7]
Potentiometry titration	Sulfosuccinate Esters	[8]
Spectroscopy	Alkylbenzene sulfonates (LABS)	[4]
Spectroscopy	Alcohol Ethoxylates (AEOs)	[8]
High-Performance Liquid Chromatography (HPLC)	Linear Alkyl Benzenesulfonates (LAS)	[9]
High-Performance Liquid Chromatography (HPLC)	Cetyltrimethylammonium bromide (CTAB)	[8]

Spectrophotometry measures a chemical substance's ability to absorb light at specific wavelengths by measuring light intensity as it travels through a sample solution [10]. This is dependent on the concentration of the chemical component. Each substance absorbs light within a specific spectrum of wavelengths. The standard reference technique for AS determination in environmental samples uses methylene blue and chloroform. The blue-coloured chloroform soluble ion-pair complex known as the methylene blue active substance (MBAS), which is created when AS and methylene blue combine, is analysed using a colourimetric technique [11]. The traditional AS analytical approach is labour- and time-intensive due to chloroform's low AS extraction efficiency and other limiting characteristics, such as its high density and volatility. Apart from that chloroform has been shown to be carcinogenic to humans and hazardous to reproduction. It irritates the skin and eyes as well [12].

Furthermore, Methylene Blue (MB) dye poses a health risk to humans above a specific threshold due to its high toxicity. It can be harmful to human health and the environment, as it is poisonous, carcinogenic, and non-biodegradable.

In this study, Copper (II) Bromide is meant to replace cationic dyes used in the spectrophotometric method without liquid-liquid extraction as the use of toxic solvents such as chloroform can be avoided. Owing to the ability of metal salts, such as copper (II) bromide, which was examined and chosen by the study due to its stability, good contact, and reactivity with SDS at varied concentrations [10]. Yet, the main focus of this study is to investigate the effect of pH towards copper (II) bromide reaction in surfactant determination. This research is the first step towards developing chemical sensors that can identify compounds in a variety of environments and comprehend chemical interactions, particularly the function of pH, which is essential to improving their effectiveness. It is discovered that there is a relationship between pH and the formation of ion pairing between SDS and copper (II) bromide ions, which is studied to affect the absorbance value.

2. Methodology

The reagents and solutions used include SDS (an anionic surfactant), TEA (an organic solvent), and copper (II) bromide, which were prepared at varying pH levels and concentrations. Additionally, chemicals such as sodium hydroxide and hydrochloric acid were utilised to adjust the pH values of the solutions.

2.1 Preparation of SDS in different concentrations

The concentration of 24 mM SDS stock solution was prepared in a 1000 mL volumetric flask by weighing 6.9211 g SDS powder as calculated using Equation 1 and Equation 2. Next, the weighed SDS powder was added into the volumetric flask with deionized water (DI) until it reached the calibration mark. The volumetric flask was carefully shaken to make sure the solution was mixed evenly. Another stock solution of 1 mM SDS was prepared in a 1000 mL volumetric flask by pipetting 41.67 mL of the 24 mM SDS stock solution. The stock solution of 1 mM concentration of SDS was then diluted into 100 ml volumetric flasks to prepare 0.05 mM, 0.10 mM, 0.15 mM, 0.20 mM, 0.25 mM, and 0.5 mM concentrations of SDS using Equation 3.

Equation to calculate the number of moles,

$$n = CV \tag{1}$$

Where C is the concentration (M) and V is the volume (L)

Equation to calculate the mass needed,

$$\text{Mass (g)} = \text{Molar Mass (g/mol)} \times \text{Number of Moles (mol)} \tag{2}$$

Equation to calculate the volume for dilution,

$$M_1V_1 = M_2V_2 \tag{3}$$

Where M_1 is the initial concentration (mM), V_1 is the initial volume (mL), M_2 is the final concentration (mM) and V_2 is the final volume (mL)

2.2 Preparation of Copper (II) Bromide metal salt stock solution

The 5 mM concentration of $CuBr_2$ stock solution was prepared by weighing 0.2792 g $CuBr_2$ black metal salt. The weighed $CuBr_2$ metal was then added into a 250 ml volumetric flask with DI until it reached the calibration mark. A light blue-coloured solution was observed after the volumetric flask containing the mix of $CuBr_2$ metal and DI was shaken to make sure the solution was mixed evenly.

2.3 Preparation of Triethylamine (TEA) stock solution

The stock solution of 5mM Triethylamine (TEA) concentration was prepared by pipetting 0.173 mL of TEA liquid into a 250 ml volumetric flask and DI was added until it reached the calibrated mark. The solution containing TEA liquid and DI were shaken thoroughly.

2.4 Determination of absorbance value for the reaction between $CuBr_2$, SDS and TEA

A volume of 1 mL of 5 mM $CuBr_2$ and 1 mL of 0.05 mM SDS was pipetted into a cuvette and mixed using a dropper. Subsequently, 1 mL of 5 mM TEA was added to the solution in the cuvette and mixed with the dropper.

Before placing the cuvette into the UV-Vis spectrophotometer, it was wiped with soft tissue. The absorbance values were then measured across the wavelength range of 400 nm to 800 nm. A graph of absorbance versus wavelength was generated, and the results were recorded. The procedure was repeated using SDS concentrations of 0.10 mM, 0.15 mM, 0.20 mM, 0.25 mM, and 0.50 mM.

2.5 Preparation of hydrochloric acid (HCl) and sodium hydroxide (NaOH)

A 0.5 M NaOH solution was prepared by weighing 2 g of NaOH pellets on an analytical balance and dissolving them in 80 mL of deionized water in a 100 mL volumetric flask. The solution was shaken and allowed to cool. Deionized water was then added to reach the calibration mark, and the flask was shaken again. The prepared solution was transferred to a glass bottle, sealed with parafilm, and labelled. Since the dissolution of NaOH in water is highly exothermic, stirring must begin immediately upon adding water to prevent localized hot spots in the container. Similarly, a 0.5 M HCl solution was prepared by diluting concentrated 37% HCl (12 M) into 0.5 M. First, 4 mL of concentrated HCl was pipetted gradually into a 100 mL volumetric flask containing deionized water while shaking. Deionized water was then added to reach the calibration mark, and the solution was shaken. Finally, the solution was transferred to a glass bottle, sealed with parafilm, and labelled.

2.6 Determination of absorbance value for the reaction between $CuBr_2$, SDS and TEA in different pH

A specific volume of 0.5 M HCl and 0.5 M NaOH was pipetted into the 100 mL volumetric flask with only one drop to alter the pH after four sets of each 0.10 mM and 0.20 mM SDS concentration were diluted from the 1 mM stock solution. Trial and error was used to get the pH of 4 and 10 on deionised water, which has a pH of about the same as SDS solution, 6. The trial-and-error results were applied to both 0.10 mM and 0.20 mM SDS solutions in order to obtain a more accurate result. After some experimentation, the 0.10 mM and 0.20 mM SDS solutions required 28 µl HCl and 50 µl NaOH to go to pH 4 and then back to their starting pH, 6. 29 µl HCl and 50 µl NaOH were required, nevertheless, to get the 0.10 mM and 0.20 mM SDS solutions back to their starting pH of 6. Before adding the DI once more until it reached the calibration line, each volumetric flask was gently shaken. After giving each set's pH-adjusted solution another gentle shake, they were moved to 50 mL beakers, pipetted for 1 mL, combined with 1 mL $CuBr_2$ and 1 mL TEA in the cuvette, and then run through a UV-Vis Spectrophotometer to measure the absorbance value between 400 and 800 nm in wavelength. Using a Hanna portable pH meter, the final pH of the residual pH-adjusted SDS solution in the beakers was determined and noted.

3. Result and Discussion

3.1 Standard calibration curve of SDS reaction with Copper (II) Bromide and TEA

Following sample testing using a UV-Vis Spectrophotometer, the absorbance values for SDS concentrations ranging from 0.05 to 0.5 mM were tabulated in Table 3. The linearity range of each SDS concentration in an aqueous solution mixed with Copper (II) Bromide and TEA is depicted in Figure 1, absorbance versus concentration linearity graph at 650 nm wavelength.

Table 3: SDS concentration and absorbance value at 650 nm wavelength

Concentration (mM)	Absorbance
0.05	0.069
0.10	0.071
0.15	0.071
0.20	0.075
0.25	0.081
0.50	0.117

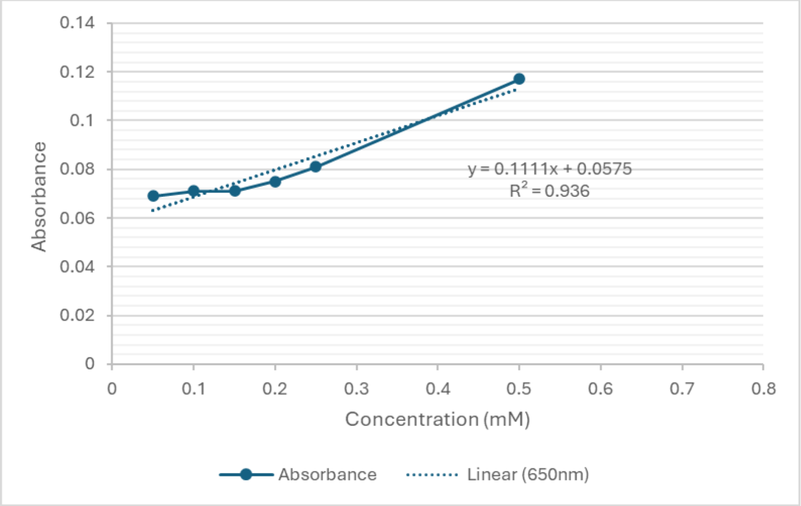

Fig. 1: Absorbance vs Concentration of SDS for Copper (II) Bromide

As a result, the graph obtained demonstrates a clear positive linear correlation between concentration and absorbance. As the concentration rises, the absorbance increases proportionally. The linear equation obtained from the base fit line produced is $y = 0.1111x + 0.0575$, and the R^2 value obtained from the graph is 0.936.

3.2 Determination of final concentration based on the linear equation obtained

The actual concentration (x-axis) derived from the linear equation by replacing the absorbance (y-axis) is also displayed in Table 4. The results suggest that higher pH levels may lead to higher absorbance and final concentrations, which could indicate the substance's pH-dependent solubility or reaction efficiency.

Table 4: Actual concentration (x-axis) obtained from the linear equation by substituting the absorbance (y-axis)

Prepared Concentration (mM)	pH	Average Absorbance, y (at 650 nm)	Final Concentration, x (mM)
0.10	4	0.100	0.3825
	6	0.080	0.2025
	10	0.104	0.4185
0.20	4	0.112	0.4905
	6	0.091	0.3015
	10	0.120	0.5626

Table 5: Comparison of the absorbance value and final concentration between the adjusted sample and readjusted pH sample

Concentration (mM)	pH	Adjusted sample to required pH		pH	Re-adjusted pH sample to pH 6	
		Absorbance value	x		Absorbance value	x
0.10	4	0.085	0.2467	6	0.100	0.3825
	6	0.069	0.1042	6	0.080	0.2025
	10	0.091	0.3001	6	0.104	0.4185
0.20	4	0.091	0.3001	6	0.112	0.4905
	6	0.077	0.1754	6	0.091	0.3015
	10	0.094	0.3268	6	0.120	0.5626

Based on the result in Table 5, the absorbance values and final concentrations are consistently higher in the readjusted pH sample condition for both the 0.10 mM and 0.20 mM concentration levels. A diluted solution's absorbance is low because there are fewer molecules available to interact with light [10]. Yet, the addition of hydrochloric acid and sodium hydroxide causes the absorbance value to be higher than the pure SDS solution. As the pH of the surfactant solution rises, the amount of hydroxyl groups on the surface decreases, which affects hydrogen bond formation [13]. As a result, several interferents impact anionic surfactant detection, such as chlorine ions and hydroxide ions [14].

The ions from HCl (H^+ and Cl^-) or NaOH (N^+ and OH^-) could chemically interact with the solute in the solution, forming complexes or changing the electronic structure. This could alter the way the molecules absorb light, leading to increased absorbance. Because the ions influence solvation and hydrogen bonding, this interaction may result in spectrum shifts and modifications to the absorption properties. Changes in the electronic environment of the chromophores may cause variations in the absorption spectra due to the disruption of hydrogen bonding networks caused by HCl in solution [15]. According to Sasaki and Okabe (2011), NaOH tends to make compounds more soluble in aqueous solutions, raising chromophores' concentration and providing more noticeable absorption characteristics. It makes sense when the absorbance value for the SDS concentration with pH 10 was higher than pH 4.

Despite its limitations, this research approach presents a viable substitute for conventional approaches. Only when using pure water samples that contain SDS and a pH of 6 does it work well. Copper (II) bromide and TEA can be interfered with by other ions, like those present in water samples from drains close to the cafeteria, which can affect the precision of the results.

4. Conclusion

The study successfully investigated the effects of pH on the Copper (II) Bromide reaction in surfactant determination. A strong linear relationship ($R^2=0.936$) was established between absorbance and concentration at 650 nm, with the equation $y=0.1111x + 0.0575$. The optimal pH for SDS ion-pairing was identified as pH 6, showing the most consistent absorbance. Maintaining stable pH conditions and performing triplicate pH testing is recommended to enhance accuracy.

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Conflict of Interest

Author declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

This journal requires that all authors take public responsibility for the content of the work submitted for review.

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