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

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Abstract

Surfactants in cleaning products harm water quality. Anionic surfactants (AS) are particularly harmful. The current method to detect AS is difficult and requires toxic solvents. A new spectrophotometric method is needed to quickly and easily detect AS in water. This study employed copper (II) bromide metal salts because to their colour, water solubility, and stability. Utilizing the influence of pH on the reaction between certain Copper (II) Bromide ($CuBr_2$) metal salts, Sodium Dodecyl Sulphate (SDS), and Triethylamine (TEA), the absorbance value at 650 nm wavelength is determined, and a calibration curve is created. The linear equation y = 0.2528x + 0.0246, is used to calculate SDS concentration from absorbance at various pH levels, with a very accurate fit indicated by an R^2 of 0.9974. The study aims to determine the ideal pH range that guarantees, building on the effective usage of CuBr2 in surfactant testing. The study involves a thorough examination of the indicator's performance under varied pH conditions, aiming to enhance the reliability of results and improve the ability to detect surfactants at various concentrations. From this study, the result shows that the shifted pH change the concentration of surfactant in the water sample. There is a small variation in the concentration measurement at pH 4 between the initial concentration of 0.1 and 30%, which is 0.1 to 0.7. This indicates that the surfactant's behavior is sensitive to pH changes. The change is relatively slight. It suggests that the surfactant's efficacy or behavior might be altered in this pH environment, possibly affecting its cleaning ability, toxicity, or interaction with other chemicals or biological entities in the water.

1.0 Introduction

Surfactants are a class of compounds widely used in various industries, including detergents, personal care products, and agrochemicals, due to their ability to lower the surface tension of liquids. Surfactants are among the most challenging emerging contaminants which are continuously discharged into the environment through wastewater treatment plants (WWTPs). Surfactants are employed for various domestic and industrial applications due to their unique physicochemical properties [1]. Surfactants can be found in various types of water in different environments, including laundry, car washes, kitchens, and domestic settings including sea and river. Surfactants, including anionic surfactants, can have biological effects when they come into contact with living organisms. These effects can vary depending on the specific surfactant, its concentration, exposure duration, and the type of organism involved. Among surfactants' main biological impacts are toxicity, irritation and sensitization,

respiratory effects, environmental disruption and bioaccumulation. Surfactants have two types of impacts on the human body which are those on the skin and those that penetrate the body. Surfactants are the most common chemicals in modern detergents, and long-term use can cause skin irritation and damage [4]. Surfactants enter the human body and disturb the body's regular physiological function by damaging enzyme functioning. The concentration of surfactant can be found by using the standard current method which is methylene blue active substances (MBAS), but this method involves the use of hazardous substances such as chloroform and methylene blue that have serious effects on human health. this study found the most suitable method for the determination of anionic surfactants, but it was modified and adjusted to work in a continuous flow system combined with spectrophotometric measurement. Spectrophotometric methods typically was found to be satisfactory in terms of sensitivity and precision, with a short time to analysis. In this study, $CuBr_2$ metal salts were chosen because of its color, solubility in water, stability and good performance compared to other metal salts. The interaction between selected $CuBr_2$ metal salts, sodium dodecyl sulphate (SDS) and triethylamine (TEA) with the influence of pH is used as the method to obtain absorbance value at 650 nm wavelength. This research study objective aims to construct the calibration curve of copper (II) bromide against anionic surfactant concentrations. Then, to determine the response to copper (II) bromide metal salts towards different pH range from pH 4,5,7 and 8 in synthetic water sample. Last but not least, to relate the effect of pH4, pH5, pH7 and pH8 changing in the determination of surfactant using copper (II) bromide method response.

2.0 Methodology

The study began by weighing 0.1137 g of CuBr2, which was then diluted in a 250 mL volumetric flask to prepare a 5 mM concentration of CuBr2 stock solution. Subsequently, a stock solution of TEA with a concentration of 5 mM was produced using 0.173 mL of TEA liquid, pipetted with a micropipette into a 250 mL volumetric flask in a fume hood. Following this, 0.28838 g of SDS powder was weighed and diluted with deionized water (DI), and the resulting solution was added to a 1000 mL volumetric flask to create samples with concentrations of 0.02 mM, 0.04 mM, 0.06 mM, 0.08 mM, 0.10 mM, 0.15 mM, and 0.2 mM of SDS in 100 mL volumetric flasks. These samples were tested alongside TEA and CuBr2 for the construction of the calibration graph. Additionally, a 1 mM SDS stock solution was diluted into 100 mL volumetric flasks to prepare concentrations of 0.05 mM, 0.15 mM, and 0.4 mM SDS. The NaOH and HCl solutions were then prepared to achieve the targeted pH for SDS from the initial pH. For the NaOH solution, 2 g of NaOH pellets were weighed on an analytical balance and dissolved in 80 mL of DI in a 100 mL volumetric flask, and the mixture was shaken. After the NaOH solution cooled down, DI was added again until it reached the calibration mark, and it was shaken. A diluted concentration of 0.5 M Hydrochloric acid (HCl) 33% was prepared by diluting 10.17 M of HCl to a 0.5 M concentration with the addition of 20 mL of DI.

2.1 Preparation of reagents

0.1137 g of $CuBr_2$ was diluted in a 250 mL volumetric flask to prepare a 5 mM concentration of $CuBr_2$ stock solution as shown in Figure 1 below.

Figure 1: Light blue coloured solution of $CuBr_2$ in a volumetric flask

Then, a stock solution of TEA with a concentration of 5mM was produced using 0.173mL of TEA liquid, pipetted with a micropipette into a 250mL volumetric flask in a fume hood as shown in Figure 2.
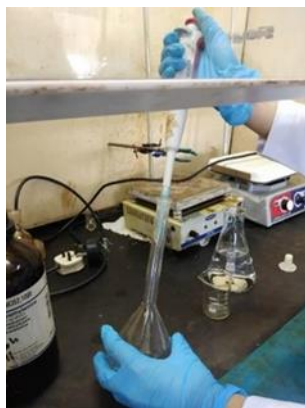
Figure 2: TEA was pipetted into volumetric flask

After that, weighing 0.28838g of SDS powder and diluted it with DI and then added to a 1000 mL volumetric flask to create samples with concentrations of 0.02mM, 0.04mM, 0.06mM, 0.08mM, 0.10mM, 0.15mM, and 0.2mM of SDS in 100mL volumetric flasks that tested along with TEA and $CuBr_2$ for the construction of the calibration graph as shown in Figure 3. Then, 1 mM SDS stock solution was diluted into 100 mL volumetric flasks to prepare concentrations of 0.05 mM, 0.15 mM, and 0.4 mM SDS.

Figure 3: Preparation of various concentration of SDS

Then, prepare the NaOH and HCl as shown in Figure 4 to obtain the SDS targeted pH from the initial pH. To prepare the NaOH solution, 2 g of NaOH pellets were weighed on an analytical balance and dissolved in 80 mL of DI in a 100 mL volumetric flask, and the mixture was shaken. After the NaOH solution cooled down, DI was added again until it reached the calibration mark and was shaken. A diluted concentration of 0.5 M HCl 33% was prepared. 10.17 M of HCl was diluted to a 0.5 M concentration by adding 20 mL of DI water.

Figure 4: Preparation of NaOH and HCl for pH adjusted

3.0 Result and Discussion

The results and discussion may fulfill the objectives for this study as the absorbance readings from standard calibration curve was proportional with the data obtained. $CuBr_2$ metal salt is to be used in this study with seven different concentrations of SDS. The graph calibration of SDS have been constructed with seven concentrations of SDS which were 0.02 mM, 0.04 mM, 0.06 mM, 0.08 mM, 0.10 mM, 0.15 mM, and 0.20mM. The concentration of SDS to be pH examined by pH shifted was 0.10 mM, 0.15 mM, and 0.20Mm.

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

The linear graph of absorbance against concentration for $CuBr_2$, SDS and TEA reaction at 650 nm wavelength were plotted based on the information in Table 1. A good linearity range of 0.02 mM - 0.20 mM SDS concentration in an aqueous solution mixed with Copper (II) Bromide and TEA is shown by the linearity graph for absorbance against concentration at 650 nm wavelength in Figure 5. The linear equation obtained from the base fit line produced is y = 0.2528x + 0.0246, and the R^2 value obtained from the graph is 0.9974.

Table 1: SDS concentration and absorbance value at 650 nm wavelength

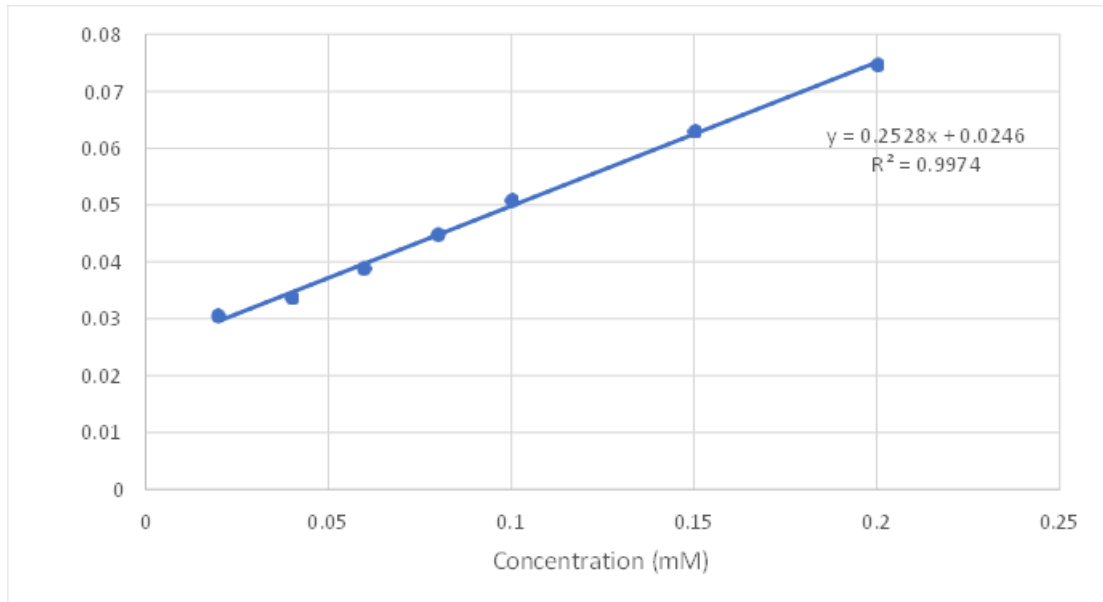| Concentration (mM)	Absorbance
0.02	0.030508
0.04	0.033696
0.06	0.038822
0.08	0.044798
0.10	0.050826
0.15	0.062935
0.20	0.074662

Figure 5: Calibration curve of absorbance against concentration of SDS at 650nm wavelength

Table 2: The various concentration of SDS in different pH from percentage deviation (%)

Concentration of SDS	Initial absorbance	Initial pH	Targeted pH	Final concentration from calibration curve (mM)	% deviation
0.10	0.050826	7.69	4	0.07123	0.3
			5	0.05635	0.5
			7	0.02819	0.8
			8	0.03372	0.7
0.10	0.050826	7.69	-	0.1037	0.37
0.15	0.062935	3.16	4	0.04841	0.73
			5	0.0549	0.67
			7	0.05656	0.67
			8	0.04121	0.73
0.15	0.062935	3.16	-	0.1516	0.16
0.20	0.074662	3.3	4	0.29363	0.45
			5	0.29754	0.45
			7	0.28983	0.4
			8	0.29905	0.5
0.20	0.074662	3.3	-	0.1980	0.2

This research indicates that the calibration curve for predicting SDS concentrations is less reliable at higher pH values, with significant deviations across all pH levels suggesting non-linear relationships and potential interference from other variables. As concentration increases, the impact of pH on absorbance decreases, hinting at other overriding factors or limited solubility/stability at higher concentrations. It was found that adjusting water sample pH affects surfactant concentration, with a 30% concentration difference at pH4 and 0.1 concentration being the most effective condition identified.

5.0 Conclusion

The study successfully created a calibration curve for $CuBr_2$ interaction with anionic surfactants, particularly SDS and TEA, achieving high linearity ($R^2 = 0.9974$) at a wavelength of 650nm. Without pH adjustment, the percentage deviation reading is between 0.16%-0.37% for concentrations of 0.10 mM, 0.15 mM, and 0.20mM. But when the pH is adjusted, the percentage deviation changes by 0.2%–0.8%. It is possible that HCl and NaOH have an impact on $CuBr_2$ and the SDS reaction. Since they are unable to interpret the SDS concentration, the Cl^- and OH^- ions in the adjuster create complex metals that have an impact to a greater percentage deviation compared to the original SDS concentration.

Acknowledgement

References

[1] Artur Seweryn (2018). Interactions between surfactants and the skin – Theory and practice. http://dx.doi.org/10.1016/j.cis.2018.04.002

[2] Cornwell, P. A. (2018). A review of shampoo surfactant technology: consumer benefits, raw materials and recent developments. International journal of cosmetic science, 40(1), 16-30. https://onlinelibrary.wiley.com/doi/abs/10.1111/ics.12439

[3] Hatley, H. (2018) The role of surfactants in wastewater treatment:Impact,removal and future techniques: A critical review. Water Research, 147, 60–72. Elsevier Ltd. https://www.sciencedirect.com/science/article/pii/S0043135418307541

[4] Ramprasad, C., & Philip, L. (2016). Surfactants and personal care products removal in pilot scale horizontal and vertical flow constructed wetlands while treating greywater. Chemical Engineering Journal, 284, 458-468. https://www.sciencedirect.com/science/article/pii/S1385894715011742

[5] Seweryn, A. (2018) Interactions between surfactants and the skin – Theory and practice. https://www.sciencedirect.com/science/article/pii/S0001868617305250

[6] Stuart R Gallant, Vish Koppaka, Nick Zecherle (2008). Dye ligand chromatography. https://pubmed.ncbi.nlm.nih.gov/18826048/

[7] Surfactants in a Wastewater Treatment Plant of Algiers Western Region by a Simplified Spectrophotometric Method. Journal of Surfactants and Detergents, 19(6), 1305–1314. https://doi.org/10.1007/s11743- 016-1884-x

[8] Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental science & technology, 37(20), 4702-4708. https://pubs.acs.org/doi/abs/10.1021/es030360x

[9] ZA Shoaibi, AA Gouda (2012). Extractive Spectrophotometric Method for the Determination of Tropicamide. Retrieved from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3326782/