PROGRESS IN ENGINEERING APPLICATION AND TECHNOLOGY
e-ISSN: 2773-5303

PEAT

Vol. 5 No. 1(2024) 526-534
https://publisher.uthm.edu.my/periodicals/index.php/peat

Effects of Anion Presence to Copper (II) Bromide Response Towards Anionic Surfactant in Water Sample

Ahmad Waliyuddin Nor Asri[1], Nor Haslina Hashim[1]*

[1] *Department of Civil Engineering Technology, Faculty of Engineering Technology University Tun Hussein Onn Malaysia, Pagoh Higher Education Hub, 84600 Panchor, Johor, Malaysia*

*Corresponding Author: haslina@uthm.edu.my
DOI: https://doi.org/10.30880/peat.2024.05.01.055

Article Info

Received: 28 December 2023
Accepted: 10 January 2024
Available online: 15 June 2024

Keywords

Anionic surfactant, Copper (II) Bromide, Sodium Dodecyl Sulfate, Absorbance, Anion salt

Abstract

Maintaining cleanliness in our daily lives involves the use of cleaning agents, often containing surface-active agents or surfactants, which play a crucial role in various industries. Despite their widespread use, the environmental impact of surfactants, specifically anionic surfactants, has raised concerns due to their poor biodegradability and various adverse on ecosystems. Previous research has shown that Copper (II) Bromide, $CuBr_2$, could possess the potential to detect anionic surfactant in water sample. There is various factor that needs to be addressed before confirmation regarding the ability of $CuBr_2$ to detect anionic surfactant can be determined. This is due to countless factor that may occur in real-life situation that may affect the credibility of this new proposed method. Methylene Blue Active Substance (MBAS) method is the well establish technique that is used to detect anionic surfactant at the moment. However, this method is time-consuming and employs the use of toxic chemical which is chloroform to extract the solution. Therefore, this study aims to find out the ability of $CuBr_2$ to detect anionic surfactant in presence of anion in the same water sample to anticipate one of the various scenarios that may occur in real-life situation. This study comprises of laboratory investigation that uses Sodium Dodecyl Sulfate (SDS) as the anionic surfactant, Triethylamine (TEA) as organic solvent and multiple anion samples which were chloride ion, nitrate ion and sulphate ion to observe the response of $CuBr_2$ towards the presence of anion and anionic surfactant in the same water sample. A calibration curve was constructed with R^2 value of 0.9752 and equation of $y = 0.098x + 0.0303$ which was used to determine the final concentration of each SDS sample that was mixed with 4mM and 8mM of anion individually. The result shows that, the presence of anion in the water sample reduce the absorbance value of the sample. The mixing of SDS and anion in the sample form a metal complex resulting in $CuBr_2$ unable to react with SDS in the sample. This indicates that $CuBr_2$ can only directly detect anionic surfactant precisely if there is no other anion element in the water sample. It can be concluded that this method is non-selective towards anionic surfactant.

1. Introduction

When it comes to the requirements of everyday life, keeping our surroundings tidy and making sure our clothing is clean are essential parts of our routine. Although most people are aware of how to utilize standard cleaning supplies like soap and detergent, surface-active agents, or surfactants, have a complex role that is sometimes disregarded [1]. These chemicals are essential to many different industries, including the automotive, industrial, textile, cosmetic, and food sectors. They are also widely used in personal care products. Surfactants are amphiphilic substances that may lower surface tension between liquid, gas, and solid phases. They are identified by a polar soluble head group and a nonpolar hydrocarbon tail. Each of the four groups of surfactants—cationic, amphoteric, non-ionic, and anionic—has unique properties and uses [2].

With their negatively charged heads, anionic surfactants are excellent in eliminating organic contaminants such as grease and oil from detergents and soaps, whereas cationic surfactants, on the other hand, have positively charged heads and work well as disinfectants. Amphoteric surfactants are zwitterionic substances with both positive and negative charges; their behaviour is dependent on the pH of the material they interact with [4]. Because they don't have a charge on their hydrophilic end, nonionic surfactants are good at emulsifying oils and fats and are frequently used with anionic surfactants. However, the widespread usage of these surfactants—particularly anionic surfactants—contributes greatly to pollution of the environment, leading to problems including water and soil contamination.

Stormwater runoff, residential areas, industrial discharges, wastewater treatment plants, and even sewage sludge used as fertiliser are the main sources of surfactants in the environment. Because anionic surfactants effect on the environment, it is important to detect them using a variety of techniques, including titration, spectrophotometry, and High-Performance Liquid Chromatography (HPLC) [3]. However, these methods have their challenges, with the Methylene Blue Active Substance (MBAS) method being commonly used despite its limitations [5]. Notably, certain detection techniques include dangerous substances like chloroform, which calls for cautiousness and specialised tools. To avoid the use of dangerous chemicals like methylene blue and chloroform in further studies, the study suggests using $CuBr_2$ as a potential breakthrough in surfactant detection. $CuBr_2$ selectivity and sensitivity are being investigated in this study by evaluating its capacity to react with anionic surfactants in water samples containing anions. The fundamental goal of the study is to enhance the field of surfactant detection, specifically in water samples with anionic presence. This is what the experiment ultimately seeks to accomplish.

2. Methodology

All the reagents required for this study was prepared priorly before the experiment is conducted. Firstly, different concentration of SDS (0.04mM, 0.05mM, 0.06mM, 0.1mM, 0.15mM, 0.2mM and 0.5mM) for construction of calibration graph was prepared. Then, SDS concentration (0.05mM, 0.06mM, 0.1mM, 0.15mM and 0.2mM) that was tested along with other solution namely, $CuBr_2$, TEA and different anions sample was prepared. Next, stock solution of TEA in concentration of 5mM was made in 250mL volumetric flask. The appropriate volume of TEA, which is 0.174 mL was first pipetted into the flask and then deionized water were added. For $CuBr_2$, the stock solution was also prepared in 5mM concentration which uses 0.2792g of its powder. Lastly, for anion samples, each of the three which is chloride ion, sulphate ion and nitrate ion were prepared in 4mM and 8mM concentration respectively.

2.1 Preparation of Different type of Anion sample Along with SDS

For preparation of chloride ion in 4mM concentration, 0.0234g of sodium chloride, NaCl, was weighted and inserted into a 100mL volumetric flask that contains SDS sample in various concentration. The mass required was calculated. Then, deionized water was added until it reached the calibrated mark. It is also the same case for 8mM concentration, the only difference was the mass of anion sample inserted into the volumetric flask that contains SDS concentration. The preparation step was repeated for preparing nitrate ion using potassium nitrate, KNO_3, and sulphate ion using sodium sulphate, Na_2SO_4. Figure 1 below shows prepared SDS solution in various concentrations with anion sample in each of it. Figure 1 shows mixture various concentration of SDS with anion sample.

Fig. 1: *Mixture of SDS in various concentration with anion*.

2.2 Determination of Calibration Graph

To construct the calibration graph, seven sets of 1mL SDS sample that has been prepared earlier with concentration of 0.04mM, 0.05mM, 0.06mM, 0.1mM, 0.15mM, 0.2mM and 0.5mM were mixed with 1ml of TEA and 1mL of $CuBr_2$ both with 5mM concentration. By using micropipette, SDS sample and $CuBr_2$ sample was inserted into a cuvette and mixed well using a dropper. Then, the TEA solution was added and mixed with dropper. Before the cuvette is inserted into the UV-Vis Spectrophotometer, it was wiped first using a soft tissue. The reading for absorbance values for wavelength range of 400nm – 800nm was recorded.

2.3 Determination of Anion Effect on SDS Concentration

First, sample of 4mM NaCl was prepared in 100 mL volumetric flask, followed by 5mM of $CuBr_2$ and 5mM of TEA solution. Then, 1mL of each sample was placed in a cuvette glass respectively by order. Next, the cuvette glass was wiped using a soft tissue to ensure the surface is clear. Then, the cuvette glass was placed in the UV-Vis Spectrophotometer to read the absorbance value for wavelength in range 400 nm – 800 nm. The data was recorded in a compact disc to be further analysed.

The effect of SDS response towards $CuBr_2$ in presence of other anion namely Cl^-, NO_3^- and SO_4^- by embedding this anions in the water sample along with SDS, and then tested with $CuBr_2$. The SDS that was prepared in 0.05 mM, 0.06 mM, 0.1 mM, 0.15 mM and 0.2 mM was tweaked by adding powder of each anion salt in the volumetric flask before it was fully mixed. The mass of the anion salt was equivalent to 4mM and 8mM of the prepared anion solution that was used to determine the effect of individual anion solution to the response of $CuBr_2$ earlier. The step required to obtain absorbance value was same as the paragraph above.

3. Results and Discussion

3.1 Construction of Calibration Curve

First, sample of SDS in 0.04 mM, 0.05 mM, 0.06 mM, 0.1 mM, 0.15 mM, 0.2 mM and 0.5 mM was prepared. 1mL of all these sample are inserted in cuvette glass along with 1mL of CuBr2 in 5mM and 1mL of TEA also in 5mM. The absorbance value of data in range 400 nm – 800 nm was recorded and observed. Wavelength 650 nm was chosen for refer point due to its ability to absorb better at this specific wavelength. As stated in methodology, the mixture of three different type of chemicals with three different colour will make it not viable to observe the result based on colour . Table 1 shows the data for SDS and the calibration curve that has been produced using the same data, the graph of Absorbance vs Concentration of SDS has been plotted in Figure 2. This calibration curve was constructed as the reference value to determine the response of CuBr2 in water sample that possess both anionic surfactant and anion.

Table 1: *Data for absorbance of SDS*

Concentration (mM)	Absorbance
0.04	0.032188
0.05	0.034674
0.06	0.03437
0.1	0.045028
0.15	0.043092
0.2	0.052393

0.5	0.078394

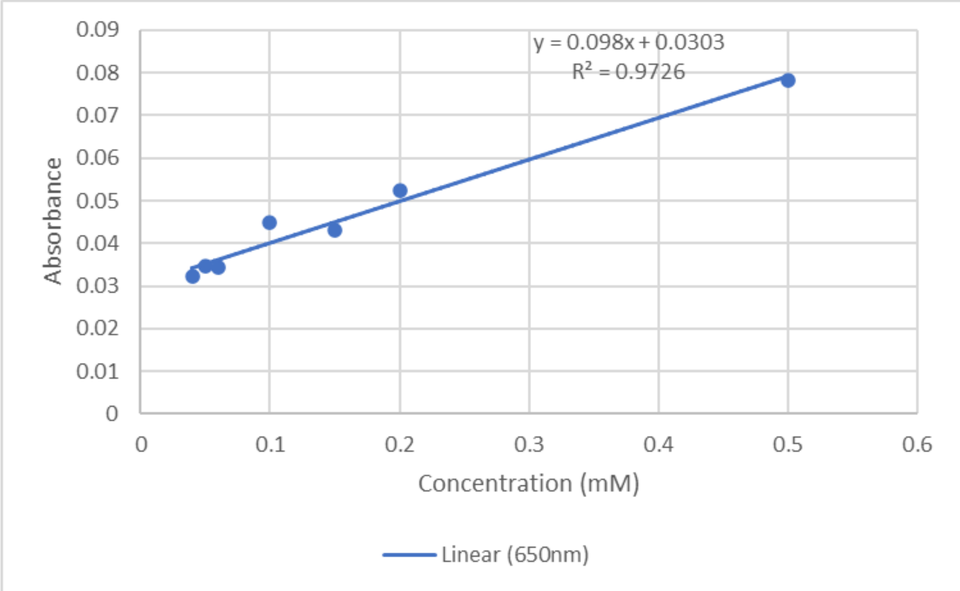

Fig 2: *Absorbance vs Concentration of SDS at 650 nm*

The R^2 value for this graph is 0.9726 while the equation is y = 0.098x + 0.0303. This equation was utilized to calculate the final concentration, *c* (mM) SDS in sample that was mixed with chloride ion, nitrate ion and sulphate in 4mM and 8mM respectively to observe the effect of anion presence towards the ability of $CuBr_2$ to detect SDS. The calibration curve was constructed as it is the standard linear line of absorbance against concentration that will be applied to predict the concentration of known absorbance from UV-Vis reading.

3.2 Determination for Effect of Anion Towards Copper (II) Bromide

As mentioned above, there were a total of three anion sample that has been tested with water sample that consist of SDS in it namely, chloride ion nitrate ion and sulphate ion. Two concentration which is 4mM and 8mM were used to observe the effect of anion towards $CuBr_2$ response. Table 2 shows the absorbance value and its final concentration that was calculated from equation y=0.098x+0.0303.

Table 2: *Final Concentration based on calibration graph for each type of anion*

Type of Anion	Anion concentration (mM)	Absorbance, y (L mol^{-1})	Final concentration, *c* (mM)
Chloride Ion	4	0.0405	0.1041
	8	0.0407	0.1061
Nitrate Ion	4	0.0248	-0.0561
	8	0.0236	-0.0684
Sulphate Ion	4	0.0378	0.0765
	8	0.0337	0.0347

The result obtained in Table 2 shows that the absorbance value for each concentration set is nearly the same with each other although the huge difference in concentration. This proves that $CuBr_2$ will not react to sample that purely possess anion. Except for chloride ion, both nitrate io and sulphate ion shows a decrease in absorbance value and ultimately the final concentration that was calculated. Hypothetically, this may occur due to difference of molar mass for each sample which is 58.44 g/mol for chloride ion, 101.10 g/mol for nitrate ion and 142.04 g/mol for sulphate ion as the trend shows that as the molar mass increase, the difference in absorbance value also increases more significantly [6].

3.3 Response of Mixture of Various Anion with SDS in Different Concentration Towards Copper (II) Bromide

All the absorbance data recorded in Table 3 was taken from wavelength 650 nm in order to match the calibration curve data. The final concentration, *c* (mM) was calculated using the equation y = 0.098x + 0,0303 obtained from calibration graph (Figure 4.1) and also recorded in Table 3.

Table 3: *Final concentration of SDS based on calibration curve for each individual anion solution*

Prepared SDS concentration (mM)	Type of anion solution	Anion concentration (mM)	Absorbance, y $(L\ mol^{-1})$	Final concentration, *c* (mM)
0.05	Chloride ion	4	0.0318	0.0153
		8	0.0310	0.0071
	Nitrate ion	4	0.0355	0.0531
		8	0.0368	0.0663
	Sulphate ion	4	0.0421	0.1204
		8	0.0437	0.1367
0.06	Chloride ion	4	0.0343	0.0403
		8	0.0331	0.0286
	Nitrate ion	4	0.0312	0.0092
		8	0.0350	0.0480
	Sulphate ion	4	0.0393	0.0918
		8	0.0442	0.1214
0.1	Chloride ion	4	0.0341	0.0388
		8	0.0336	0.0337
	Nitrate ion	4	0.0321	0.0184
		8	0.0375	0.0735
	Sulphate ion	4	0.0459	0.1592
		8	0.0590	0.2929
0.15	Chloride ion	4	0.0334	0.0316
		8	0.0343	0.0408
	Nitrate ion	4	0.0284	-0.0194
		8	0.0339	0.0367
	Sulphate ion	4	0.0415	0.1143
		8	0.0442	0.1418
0.2	Chloride ion	4	0.0388	0.0867
		8	0.0379	0.0776
	Nitrate ion	4	0.0342	0.0398
		8	0.0397	0.0959
	Sulphate ion	4	0.0425	0.1245
		8	0.0420	0.1194

Table 3 indicates that majority of data are unable to project a close concentration value to the original concentration value. Only two out of the 15 final concentration value indicates a near actual SDS value which is, 0.05 SDS and 4mM nitrate ion, and 0.15 SDS and 8mM sulphate ion. Theoretically, when SDS are mixed with compound that possess charged ion, metal complex will form. Critical micelle concentration is the point where surfactants start to form micelle and reduction in surface tension occur [7] . Addition of salts such as sodium chloride, potassium nitrate and sodium sulphate during SDS sample preparation stage cause formation of metal complex between SDS and the salt. Ultimately, disrupting $CuBr_2$ ability to form metal complex with SDS [8].

The formation of metal complex is due to ion pairing between SDS and salt presence. Ion pairing is a chemical reaction where ions with different charges combine with one another to produce a new compound in the solution. The concept of anionic surfactant using $CuBr_2$ that was previously researched, utilized a water sample that only possess SDS sample in it, thus eliminates the possibility for ion pairing between other chemicals with SDS sample before addition of $CuBr_2$ into the cuvette glass for reading. Although the absorbance value varies either higher or lower than original concentration value, it indicates that this method is not suitable for determination of anionic surfactant in the presence of other anions. Hypothetically, it happened due to competition between anion and $CuBr_2$ to combine with SDS in the water sample [9].

3.4 Effect of Anion Presence Towards Absorbance Value of $CuBr_2$

According to Figure 5, the R^2 value for calibration graph, Absorbance vs Concentration of SDS is 0.9726 or 97% in precision. This graph consists of seven readings which is 0.04 mM, 0.05 mM, 0.06 mM, 0.1 mM, 0.15mM, 0.2 mM and 0.5 mM. The reason for the extra two readings was to predict the movement of linear line outside tested concentration range. As the value of R^2 become closer to 100%, the movement of dependent variables become more relatable to movement of changed variables. From the graph, the equation of y=0.098x+0.0303 was obtained where it was utilised for calculation of final concentration, *c* (mM) of SDS in all sample that was tested. X-axis of Figure 3, Figure 4 and Figure 5 is the concentration of SDS in data where 1 represents 0.05 mM, 2 represents 0.06 mM, 3 represents 0.1 mM, 4 represents 0.15 mM and 5 represents 0.2 mM.

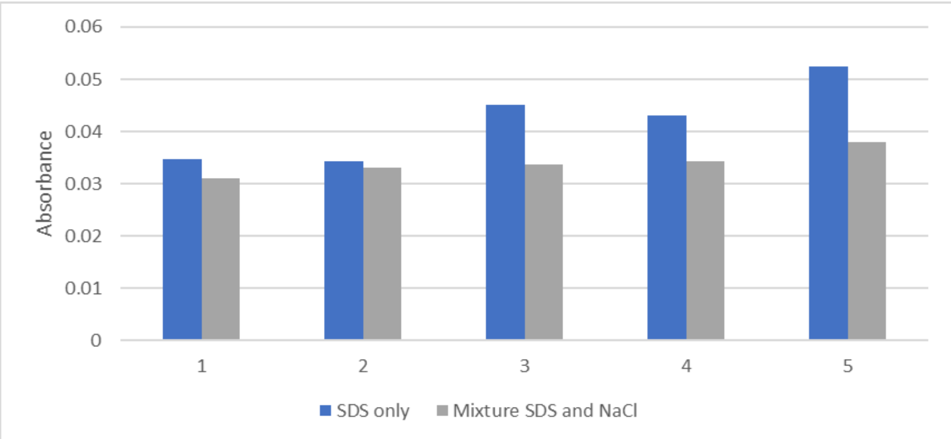

Fig. 3: *Comparison graph of absorbance value between sample that contains only SDS and mixture of NaCl and SDS*

Figure 3 shows that difference in value of absorbance between sample that only contain SDS and sample that contains SDS and NaCl. The trend indicates that presence of chloride ion reduces the absorbance of $CuBr_2$ towards SDS. Again, these may happen because of ion pairing between SDS and NaCl before addition with $CuBr_2$. Metal complex formed cause disturbance in $CuBr_2$ ability to detect SDS in the sample. Although the concentration of chloride ion remains the same which is 8 mM for all 5 reading, we can see the value of absorbance also increases as the concentration of SDS increases. There might be a possibility of competition between anion and SDS in sample to combine with $CuBr_2$. The higher the concentration the SDS the greater the competition between SDS and anion to form a pact with $CuBr_2$.

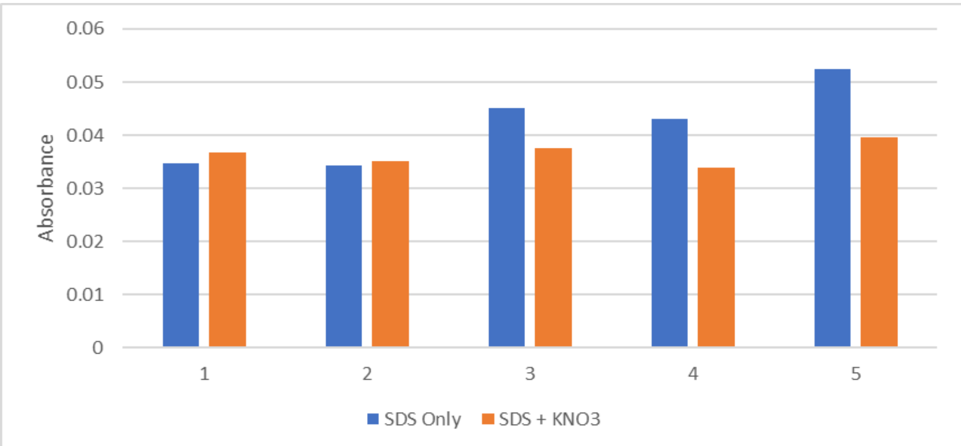

Fig. 4: *Comparison graph for absorbance value between sample that contains only SDS and mixture of SDS and KNO_3*

Figure 4 shows the difference in absorbance value between sample that only contain SDS and sample that possess both SDS and KNO_3. Most of the absorbance value for this data shows that presence of nitrate ion in sample cause reduction of SDS absorbance. Either way, to state that presence of anion will not affect the ability of $CuBr_2$ to detect anionic surfactant, the absorbance value for all five data that contains KNO_3 should be as close as possible to their counterpart that only possess SDS as in data 2 from Figure 4. Again, the trend indicates that there is competition between KNO_3 and SDS. Also, even though the concentration of anion in each sample is constant which is 8mM, the trend of absorbance also increases as if it tries to match with the concentration of SDS in sample. Compared to sample that possess chloride ion and SDS in Figure 3, the value of absorbance for nitrate ion and SDS are greater. This may indicate that difference of molar mass between anion sample affect the absorbance ability of $CuBr_2$. As the molar mass increase, the required mass of anion to produce specific concentration also increases. This strengthens the possibility of molar mass affecting the absorbance value recorded.

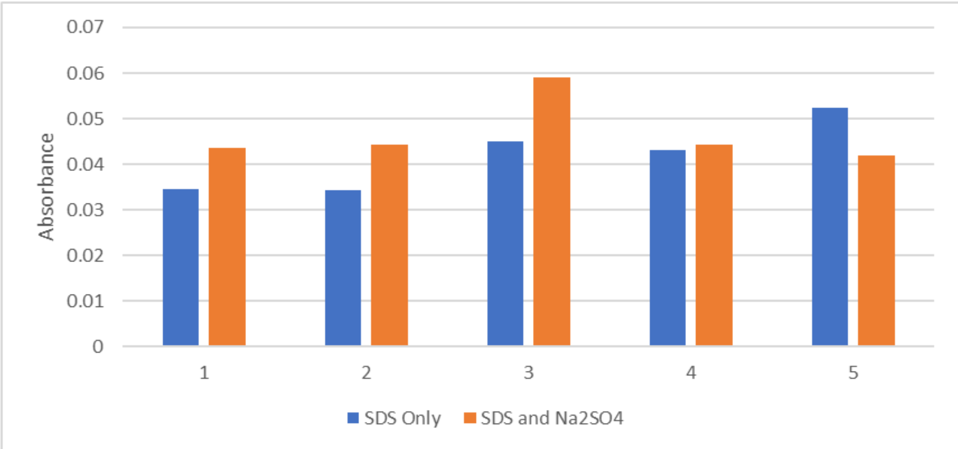

Fig. 5:*Comparison graph for absorbance value between sample that contains only SDS and mixture of SDS and Na_2SO_4*

Figure 5 shows the bar chart that compares the absorbance value of sample that only contain SDS and sample that have both SDS and Na_2SO_4. Compared to Figure 3 and Figure 4, this data shows an increase in absorbance value of $CuBr_2$ when Na_2SO_4 was mixed with SDS sample in various concentration except for data 5. A sudden spike in data 3 are due to human error that occurred during sample reading. Some examples of the causes were the mixture of sample are not mixed well, the cuvette glass is not cleaned properly before addition of next sample or the cuvette glass are not wiped thoroughly before inserted into UV-Vis spectrophotometer. However, the trend remains that as the concentration of SDS in sample that contains anion increases, the absorbance value also increases. The only difference for Na_2SO_4 is most absorbance value is greater than absorbance value of sample that only contains SDS. At the end, Figure 5 also portrays that addition of anion into water sample that contain SDS disrupts the ability of $CuBr_2$ to detect SDS in the sample. Once again, it may happen due to competition between SDS and sulphate ion to combine with $CuBr_2$ making the absorbance reading to fluctuate and ultimately unable to obtain absorbance value as in calibration curve.

4. Conclusion

A calibration graph was constructed to determine the influence of anions in water samples on CuBr2's capability to detect anionic surfactants, obtaining an R^2 value of 0.9726 at a wavelength of 650 nm. According to the 97% accurate calibration graph, the content of anionic surfactants in water samples is correlated with absorbance values. Remarkably, even with significant concentration changes (4 mM and 8 mM), the presence of chloride, nitrate, and sulphate ions alone in water samples does not alter the absorbance readings of $CuBr_2$. The study investigates the impact of anions on $CuBr_2$'s capacity to detect anionic surfactants using the derived equation $y=0.098x+0.0303$. It finds that the presence of anions impairs precision, with 28 out of 30 readings failing to achieve final concentration values close to the initial SDS concentration. When the water sample only includes anionic surfactants, the method works well. $CuBr_2$'s non-selective behaviour when additional anions are present, however, restricts its use to samples that are verified to contain solely anionic surfactants.

Acknowledgement

The author would also like to express his gratitude to Department of Civil Engineering Technology, Faculty of Engineering Technology and Tun Hussein Onn University for its support.

References

[1] Ivanković, T., & Hrenović, J. (2010). Surfactants in the Environment. *Archives of Industrial Hygiene and Toxicology*, *61*(1), 95–110. https://doi.org/10.2478/10004-1254-61-2010-1943

[2] Honciuc, A. (2021). Surfactants and amphiphiles. In *Chemistry of Functional Materials Surfaces and Interfaces* (pp. 43–77). Elsevier. https://doi.org/10.1016/B978-0-12-821059-8.00011-9

[3] Bazel, Ya. R., Antal, I. P., Lavra, V. M., & Kormosh, Zh. A. (2014). Methods for the determination of anionic surfactants. *Journal of Analytical Chemistry*, *69*(3), 211–236. https://doi.org/10.1134/S1061934814010043

[4] Nakama, Y. (2017). Surfactants. In *Cosmetic Science and Technology* (pp. 231–244). Elsevier. https://doi.org/10.1016/B978-0-12-802005-0.00015-X

[5] Kruszelnicka, I., Ginter-Kramarczyk, D., Wyrwas, B., & Idkowiak, J. (2019). Evaluation of surfactant removal efficiency in selected domestic wastewater treatment plants in Poland. *Journal of Environmental Health Science and Engineering*, *17*(2), 1257–1264. https://doi.org/10.1007/s40201-019-00387-6

[6] Hao, X., Lei, J. L., Li, N. B., & Luo, H. Q. (2014). An electrochemical sensor for sodium dodecyl sulfate detection based on anion exchange using eosin Y/polyethyleneimine modified electrode. *Analytica Chimica Acta*, *852*, 63–68. https://doi.org/10.1016/j.aca.2014.09.012

[7] Subhan, M. A., Rana, M. M., Sarker, P., & Rahman, M. A. (2016). Spectroscopic Study of Interactions of Metal Complexes, Metal Salts and Amino Acids with Anionic Surfactant Sodium Dodecyl Sulphate (SDS) Using Surfactant-Solute-PAN Dye Ternary Systems. *Journal of Scientific Research*, *8*(3), 447–461. https://doi.org/10.3329/jsr.v8i3.28182

[8] Perinelli, D. R., Cespi, M., Lorusso, N., Palmieri, G. F., Bonacucina, G., & Blasi, P. (2020). Surfactant Self-Assembling and Critical Micelle Concentration: One Approach Fits All? *Langmuir*, *36*(21), 5745–5753. https://doi.org/10.1021/acs.langmuir.0c00420

[9] Bajpai, P. (2018). Colloid and Surface Chemistry. In *Biermann's Handbook of Pulp and Paper* (pp. 381–400). Elsevier. https://doi.org/10.1016/B978-0-12-814238-7.00019-2