Influence of high pH state of Dodecylbenzenesulfonate and dissolved organic matter complex solution on the ultraviolet spectrometry of Dodecylbenzenesulfonate

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Abstract

Dodecylbenzenesulfonate (DBS) is an anionic surfactant that is the most commonly used ingredient in modern cleaning agents. Globally, billions of liters of untreated DBS are released daily into natural water bodies, which may lead to fatal consequences in micro and macro living entities, and destroy the natural ecosystem. Therefore, a simple, precise, rapid, and inexpensive method for measuring DBS is crucial for developing countries. The conventional ultraviolet (UV) spectrophotometric method cannot accurately estimate the DBS concentration in a solution containing a considerable quantity of dissolved organic matter (DOM). Recently, a new spectrometric method was developed using the 222.5 nm UV and 400 nm UV-visible (UV-vis) spectra to precisely estimate DBS concentration in the DBS–DOM complex solution. However, this newly developed method is yet to be validated under higher pH conditions. The accuracy of DBS measurements from the DBS–DOM complex solution under lower pH (5.5 and 6.5) and higher pH (12.5) conditions was compared in this study using the previously developed method. With the higher pH, the influence of the electrolyte increased the absorbance under the 222.5 nm UV spectrum. However, such influence decreased with the increase in DBS and DOM concentration. The UV-vis absorbance at 400 nm decreased under higher pH values when the DOM concentration increased, owing to the conformational change in DOM. Despite the contrasting trends of the absorbances in the two spectra, the studied method was proven to be equally applicable and efficient, even under higher pH conditions.

Keywords: Anionic surfactants, Dissolved Organic Matter, Dodecylbenzenesulfonate, High pH, UV-spectrometry, UV-vis

INTRODUCTION

Global industrialization and population growth have enhanced the use of large quantities of surfactants in domestic and commercial sectors (Park and Bielefeldt, 2003; Li et al., 2005). Recently, there has been much environmental research on the threats of surfactant-based synthetic organic pollutants in soil–water systems (Wolf & Feijtel, 1998; Cao et al., 2008; Rodriguez-Escales et al., 2012). Dodecylbenzenesulfonate (DBS), a common anionic surfactant, is a vital component in most of the currently available cleaning agents (e.g., soap, detergent, and shampoo) for personal use and industrial applications (Myers, 2005; Thiele and Nollet, 2007; Zoller, 2005; Cirelli et al., 2010; Hampel et al., 2012). Consequently, DBS is extensively used in various commercial production systems and household cleaning activities in bath soaps and detergents (Fachini et al., 2007; He et al., 1991; Inoue et al., 1978). Dispersion, emulsification, flocculation, flotation, foaming, and wettability are the major applications of DBS in industrial outlets (Myers, 2005). From a different context, DBS is one of the most widely spread pollutants found in every environmental setting, including untreated industrial effluent, sewage sludge, and solid waste (McAvoy et al., 1994; Sablayrolles et al., 2009).

Dissolved organic matter (DOM) is the largest active pool of the terrestrial carbon cycle (Kalbitz et al., 2000), which influences the decomposition, distribution, and circulation of numerous organic toxicants, such as soil pollutants, at the soil–soil solution interface (Chen et al., 2010; Huo et al., 2008; Jiang et al., 2008; Ma et al., 2001; Song et al., 2007). Generally, DOM comprises polymer-like substances and a large quantity of various organic compounds, indicating a broad range of molecular sizes and properties that typically depend on the extraction procedure (Tan, 2014; Zsolnay, 2003; Bolan et al., 2011). Humic substances comprise approximately 50 % to 75 % of the total organic matter in soil and, by extension, in DOM (Grinhut et al., 2011). Humic substances are a general class of biogenic, heterogeneous, and refractory organic compounds that occur in all terrestrial and aquatic environments

(Karavanova, 2013; Pettit, 2008; Thurman, 1985; Wetzel, 1983). Humic substances are usually categorized into three main groups, namely humic acid, fulvic acid, and humin, depending on their solubility in aqueous media (Stevenson, 1994; Fenchel et al., 2012; Kumada, 1965; Pettit, 2008). Fulvic acids have a wide pH range of solubility, while humic acids are well-soluble, except at low pH. In contrast to those two components, humin is the most insoluble in the normal pH range. Such poor solubility is mainly due to its close association with inorganic colloids, especially swelling clays and iron compounds (Ishiguro and Koopal, 2016; Cloos et al., 1981; Rice, 2001). The dark yellowish-brown to black color of DOM in an aqueous solution is because of these three principal components, and the opacity or transparency of the DOM solution depends on the quantity of dissolved humic substances and their ratio in that solution (Zhao et al., 2008).

Globally, billions of liters of DBS are released daily into different water bodies, such as canals, lakes, and rivers, from various cleaning and industrial activities (Texter, 1999; Fachini et al., 2007). According to a study by Qv and Jiang (2013), DBS exerts lethal effects on algae, and it also has a range of severely adverse effects on the survival of micro- and macro-organisms such as bacteria, phytoplankton, zooplankton, invertebrates, and numerous higher plants, which significantly threatens ecosystems (Sablayrolles et al., 2009; Kloepper-Sams et al., 1996). The tremendous amount of DBS directly discharged into the environment increases the pollutant load in the soil–water system and is also adsorbed onto the soil (Ahmed and Ishiguro, 2015). Untreated surfactant-contaminated irrigation water is extensively used in rural and undeveloped areas. This type of malpractice can adversely affect the physicochemical and biological properties of soil (Dai et al., 2001). Considering the above-mentioned concerns, an accurate, simple, rapid and low-cost measurement method to identify DBS from environmental solutions could be a vital aid to developing countries and nations.

Hossain and Ishiguro (2021) stated that the benzene group compounds of DOM might absorb ultraviolet (UV) light and be responsible for the excess quantities of DBS that are falsely measured by conventional UV spectrophotometry from a DBS-DOM complex solution. Therefore, they proposed a spectrometric method to precisely estimate DBS concentrations in aqueous solution at pH 5.0 and 6.0 that has a considerable quantity of DOM, using the UV and (UV visible) UV-vis spectra. The conjugated double-bond systems of the benzene ring in DBS and DOM were measured by their proposed method using a 222.5 nm UV spectrum together with the opacity of the DOM solution using a 400 nm UV-vis spectrum with a spectrophotometer to eliminate the influence of DOM from the measurement. However, molecular-scale spectroscopy and spectromicroscopy of the macromolecular structure have confirmed the conformation of humic substances under alkaline (pH ≥ 9.5) conditions, which may alter the absorbance characteristics of DOM at higher pH values (Chen and Schnitzer, 1976; Ghosh and Schnitzer, 1980). Therefore, it is assumed that the effect of NaOH induced elevated pH condition exhibits the influence of DOM on the absorbance characteristics of DBS-DOM complex solution, which challenges the validity of the photometric method proposed by Hossain and Ishiguro (2021) under such high pH conditions.

This study aimed to evaluate the accuracy of the measurement of dodecylbenzenesulfonate (DBS) from a DBS–DOM complex solution, under lower and higher pH conditions, using UV and UV-vis spectrometry. Because a higher pH of around 12 is sometimes used for the evaluation of humic acid characteristics, such high pH conditions were compared in this study.

MATERIALS AND METHODS

Chemicals and apparatus

The main reagent used in this study is linear sodium DBS, which is an anionic surfactant (Holmberg, 2019) with a chemical composition of $C_{12}H_{25}C_6H_4SO_3Na$ and a molecular weight

of 348.48 g/mol. The DBS was procured from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan) in white crystalline powder form, with a purity of approximately 99+ %. Sodium hydroxide (NaOH) and sodium chloride (NaCl), with a purity of 98+ %, were also procured from Fujifilm Wako Pure Chemical Corporation. A Shimadzu UV-1280 UV/UV-vis spectrophotometer was used as the primary instrument in this study.

Extraction of DOM solution

Dissolved solids (DS) were extracted from a suspension prepared with a highly humic non-allophanic Andosol from the A-horizon of the Daisen grazing ground in Tottori Prefecture, Japan. The DS were used as an index of DOM throughout this study. Schaetzl and Anderson (2005) stated that Andosols have a thick dark A-horizon with a high organic matter content. The total organic carbon content of the studied soil was measured as 13.8 %. Other physicochemical characteristics of the soil have already been reported by Ahmed and Ishiguro (2015). DOM extraction was carried out in the form of DS using two different concentrations of NaCl solution. The detailed procedure for DOM extraction was described by Hossain and Ishiguro (2021), which is similar to the salt extraction method of DOM described by Kalbitz et al. (2007). Briefly, DS was extracted with 1 mmol/L NaCl (pH 6.0) and 100 mmol/L NaCl (pH 5.0) electrolyte solutions, using a soil and electrolyte solution ratio of 1:15 (w/v, dry weight basis). The product was centrifuged and finally filtered with No.6 filter paper.

Quantification of DS

A 200 mL measure of the previously extracted DS solution from all eight different stored supernatants was oven-dried at 60 °C for 4 days (Hansen et al., 2018; Moody, 2020). The DS concentration was calculated by deducting the quantity of the dried NaCl salt. The DS

141 concentration was measured as an indicator of DOM in the solution, as it is expected to be in
142 proportion to DOM.
143
144 **Preparation of DBS–DOM complex solution**
145 The DBS–DOM complex solutions were prepared by adding the three different concentrations
146 of DBS solutions to the previously extracted DOM solution as a solvent, with eight different
147 concentrations of DS and 1 mmol NaCl/L at pH 6.0 or 100 mmol NaCl/L at pH 5.0. Triplicates
148 of 0, 50, and 500 μmol DBS/L DBS–DOM complex solutions were prepared using the
149 previously extracted and stored DS solution. A 1/100 volume of 10 w/v % NaOH was added
150 to the same number of DBS triplicates of 1 mmol/L and 100 mmol/L NaCl solutions to obtain
151 the higher pH condition (pH 12.5) of the DBS–DOM complex solutions. Hossain and Ishiguro
152 (2021) referred to such a solution as the DBS–DOM complex solution because the absorbance
153 characteristics of DBS and DOM overlap within it. DBS triplicates with no DOM were also
154 prepared together with DOM-free DBS standard solutions to obtain the DBS standard curve.
155 As the original DBS–DOM complex solutions were diluted 10 times before the
156 spectroscopic measurements, the NaCl concentrations were 0.1, and 10 mmol/L and the DBS
157 concentrations were 0, 5, and 50 μmol/L. The measured pH values of the diluted triplicates
158 were 5.5, 6.5, and 12.5 for pH 5.0, 6.0, and 12.5, respectively.
159
160 **Spectrometric measurement of absorbances using the UV and UV-vis spectra**
161 UV spectrometric measurements of DBS are usually conducted using a wavelength of around
162 ~223 nm because of the maximum detection capability in that spectrum range (Torn et al.,
163 2003; Yu et al., 2019). Therefore, a 222.5 nm light spectrum was used to measure the DBS
164 within the UV range in this study. However, 400 nm is the lowermost wavelength of the visible
165 light (400–780 nm) spectra (Lambert et al., 2014). Kumada (1965) and Sorouradin et al. (1993)

166 stated that the absorbance of humic acid is highest at the 400 nm visible light spectrum when
167 using spectrometry. We employed this 400 nm UV-vis spectrum to evaluate the opacity of the
168 DBS–DOM complex solution as an indicator of the presence of DOM. The DBS solution of
169 previously prepared triplicates was diluted 10 times with distilled water and the absorbance
170 was measured using a Shimadzu UV-1280 spectrophotometer at the 400 nm UV-vis and 222.5
171 nm UV light spectra.

172 Absorbance measures for the 10 times-diluted DOM triplicates without DBS and also the
173 similarly diluted DBS triplicates without DOM, both in lower pH (5.5 and 6.5) and higher pH
174 (12.5) conditions, were recorded under the 222.5 nm UV and 400 nm UV-vis spectra.

175

176 **Calculation of DBS concentrations**

177 To evaluate the influence of higher pH conditions of the DBS–DOM complex solution on the
178 UV spectroscopic measurement of DBS, we compared the both conventionally measured and
179 precisely calculated DBS concentrations of 10 times-diluted triplicates of DBS–DOM complex
180 solution with 0, 5, and 50 μmol DBS/L, at both higher (12.5) and lower (5.5 and 6.5) pH
181 conditions. The conventionally measured DBS concentration was directly determined using the
182 standard curve prepared in the X to Y concentration range. This standard curve was obtained
183 from the 222.5 nm UV absorbances of DOM-free DBS standard solutions having different
184 concentrations. Equation (2) is the expression of this relationship.

185 The computation of accurately calculated DBS concentration was achieved following the
186 previously proposed precise DBS estimation method of Hossain and Ishiguro (2021). Briefly,
187 they found that the absorbances measured at 222.5 nm UV and 400 nm UV-vis spectra
188 exhibited linear increases with a rise in the DS concentration. Therefore, the elimination of
189 DOM influence from the DBS-DOM complex solution was accomplished using a mathematical

model developed from the linear regression between the absorbances under 400 nm and 222.5 nm spectra.

$$y(\mathrm{DOM})=\mathrm{A}x(\mathrm{DOM})+\mathrm{B} \quad (1)$$

where, y(DOM) was the 222.5 nm absorbance, x(DOM) was the 400 nm absorbance for the DBS-free DOM solution. The standard curve of absorbance at 222.5 nm versus the DOM-free DBS concentration was obtained by using the following equation:

$$C=\mathrm{a}y(\mathrm{DBS})+\mathrm{b} \quad (2)$$

where, C was the DBS concentration, y(DBS) was the 222.5 nm absorbance of DOM-free DBS solution. Constants A, B, a, and b were obtained from standard curves. The 222.5 nm absorbance for the DBS-DOM complex solution, y(DBS+DOM), was formulated as follows:

$$y(\mathrm{DBS+DOM}) = y(\mathrm{DBS}) + y(\mathrm{DOM}) \quad (3)$$

As the DBS does not influence the 400 nm absorbance, they also found the relations as below:

$$x(\mathrm{DBS+DOM}) = x(\mathrm{DOM}) \quad (4)$$

Where x(DBS+DOM) was the 400 nm absorbance of the DBS–DOM complex solution. Finally, DOM influence was eliminated, and the precisely calculated DBS concentration (C) was obtained by placing the values of equations (1), (3), and (4) in equations (2) like below (Hossain and Ishiguro, 2021).

$$C=\mathrm{a}[y(\mathrm{DBS+DOM})-\{\mathrm{A}x(\mathrm{DBS+DOM})+\mathrm{B}\}]+\mathrm{b}$$

RESULTS

Effects of DBS and DOM on UV absorbance at 222.5 nm under different pH conditions

The influence of DS and DBS on the absorbance at 222.5 nm for different pH and NaCl conditions is plotted in Figure 1. The absorbance at the 222.5 nm UV spectrum increased in proportion to the concentrations of DS and DBS, as indicated by Hossain and Ishiguro (2021). The slopes of the linear lines were almost similar among the different DBS concentrations for

215 a specific NaCl concentration and pH condition (Fig. 1). The slopes of the linear lines ranged
216 from 0.017 to 0.018 and from 0.015 to 0.017 for pH 6.5 and pH 12.5, respectively, with 0.1
217 mmol/L NaCl (Fig. 1a). A slight decrease in the slope was observed with the decrease in DBS
218 concentration in the higher pH solution. For the solution with 10 mmol/L NaCl, the slopes
219 varied from 0.0039 to 0.0045 and from 0.0038 to 0.0045 for pH 5.5 and pH 12.5, respectively
220 (Fig. 1b). No differences were observed between the slopes for the different pH valu**es (Table**
221 1).

222 At 0.1 mmol/L NaCl, 0 mg/L DS, and 0 or 5 mmol/L DBS, the absorbance increased from
223 approximately 0.07 to 0.08 as the pH increased. The absorbance difference between solutions
224 of different pH values decreased with increasing DS and DBS concentrations (Fig. 1a).
225 Nevertheless, at 10 mM NaCl, the absorbance was always approximately 0.14 larger in
226 conditions of higher pH. No significant influence of DS and DBS concentration was observed
227 on the UV absorbances of 222.5 nm spectrum (Fig. 1b). The differences in the DBS–DOM
228 complex solution at higher and lower pH conditions remained almost identical for the different
229 concentrations of DS.

230

231 **Effect of DBS and DOM on the UV-vis absorbance at 400 nm under different pH**
232 **conditions**

233 The influence of DS and DBS on absorbance at 400 nm under different pH and NaCl conditions
234 is plotted in Figure 2. The absorbance at 400 nm in the UV-vis spectrum increased in proportion
235 to the concentration of DS. However, as indicated by Hossain and Ishiguro (2021), DBS did
236 not affect the absorbance of this spectrum. The slopes of the linear lines (DS concentration vs.
237 400 nm absorption) of certain NaCl solutions and pH values were similar to those obtained
238 with the different concentrations of DBS solutions, except for a divergence at the higher pH
239 condition with the 0.1 mmol/L NaCl solution. The slopes of the 0.1 mmol/L NaCl solution

ranged from 0.0025 to 0.0028 at pH 12.5 and 0.0032 at pH 6.5 (Table 1 and Fig. 2a). For the 10 mmol/L NaCl solution, the slopes varied from 0.00020 to 0.00022 at pH 12.5 and 0.00055 to 0.00057 at pH 5.5 ((Table 1 and Fig. 2b). The slopes decreased as the pH increased. At 0 mg/L DS, the difference in absorbance between the different pH values was either not noticed or was small and within experimental error. The results indicate that the influence of pH increased with increasing DS concentration. At 0.1 mM NaCl and pH 12.5, the slope increased as the DBS concentration increased. However, the influence of DBS on the slope was negligible under other solution conditions. Therefore, only in the 0.1 mM NaCl solution did the difference in absorbance at 400 nm between the different pH solutions become smaller when the DBS concentration increased.

Comparison between the two spectra in respect to solution pH

The absorbances of the DBS–DOM solutions for the lower and higher pH solutions at 222.5 UV and 400 nm UV-vis spectra are shown in Figure 3. A positive linear relationship between both spectra (400 nm vs. 222.5 nm absorbances) was observed regardless of NaCl and DBS concentrations or solution pH conditions in the solutions studied. The slope of the linear line was smaller in the case of the 10 mmol/L NaCl background condition compared with that in 0.1 mmol/L NaCl (Fig. 3b). The results at pH 12.5 were similar to those obtained by Hossain and Ishiguro (2021), although the relationship was slightly influenced by pH.

The 222.5 nm absorbance values at a higher pH (12.5) for the solutions with both 0.1 mmol/L and 10 mmol/L NaCl and lower DS concentration were larger than those at a lower pH. The 400 nm absorbance values at a higher pH were smaller than those at a lower pH, except for those of the 0 mg/L DS solution, as mentioned in the previous section. In light of these trends, the difference between the two regression lines for the absorbances at lower and higher pH conditions is clearly observed in Figure 3.

265 Identical slopes were noted for the specific NaCl concentration and pH condition of the
266 solution in the regression study (Fig. 3). The slopes of the linear lines of 0.1 mmol/L NaCl
267 solutions ranged from 5.5 to 5.6 at pH 6.5 and 6.0 to 6.2 at pH 12.5 (Fig. 3a). For the solution
268 with a 10 mmol/L NaCl concentration, the slopes of the regression lines varied from 7.2 to 7.7
269 at pH 5.5 and from 16 to 18 at pH 12.5 (Fig. 3b). The slopes at higher pH values were larger
270 than those at lower pH values (Table 1).

271 The coefficients of determination from the regression analyses between the DS
272 concentration and the absorbances, and between the two absorbances, are shown in Table 1.
273 The coefficients between the absorbances were relatively larger than those between the DS
274 concentration and absorbances. The linear regression line became closer to the measured data
275 when the relation was converted to 400 nm vs. 222.5 nm, compared to that of the DS
276 concentration vs. absorbance, as observed in Figures 1 to 3.

277

278 **Validation of the preciseness of the spectrometric estimation of DBS under conditions of**
279 **higher pH**

280 The relationship between the measured and actual added concentrations of DBS for the
281 different preparations of DBS–DOM complex solutions at pH 12.5, before the elimination of
282 DS influence, is plotted in Figure 4. It was revealed that the spectroscopically measured
283 concentration of DBS, using the 222.5 nm UV spectrum, was the highest for the 0.1 mmol/L
284 NaCl solution, with the maximum (34.7 mg/L) concentration of DS observed at this higher pH
285 condition (Fig. 4a). The measured DBS concentration gradually moved upward from the line
286 of the standard DBS curve with increasing DS concentration in the studied solutions. Under 10
287 mmol/L NaCl, the measured concentration of DBS also shifted upward from the standard DBS
288 curve for the different DBS–DOM complex solutions containing different quantities of DS (Fig.
289 4b). However, the deviation of the measured DBS concentrations from the true DBS

concentration line was smaller under 10 mmol/L NaCl. This is because the DS concentrations of these DBS–DOM complex solutions were far smaller than those of the 0.1 mmol/L NaCl condition due to the smaller DOM concentration.

To eliminate the influence of DOM (Fig. 4) on the accurate measurement of DBS from the solutions with a considerable quantity of DOM, we applied the photometric method proposed by Hossain and Ishiguro (2021) for the precise estimation of DBS. The calculated DBS concentration values were almost on the line of the standard DBS curve, as shown in Figure 5.

DISCUSSIONS

The absorbance characteristics of the DBS–DOM complex solution at the 222.5 nm UV and 400 nm UV-vis spectra responded differently in higher pH (12.5) than in lower pH (5.5 and 6.5) conditions. Nevertheless, we succeeded in obtaining the precise DBS concentration, while sidestepping the influence of DOM in aqueous solutions containing 0.1 mmol/L and 10 mmol/L NaCl at pH 12.5, because the elimination of the influence of DOM on the 222.5 nm UV spectrum was accomplished using the DOM solutions with the same pH.

The measured 222.5 nm UV absorbances under high pH were found to be approximately 0.14 larger for all solutions of 10 mmol/L NaCl (Fig. 1b). They were also approximately 0.007 to 0.008 larger for the solutions of 0.1 mmol/L NaCl, 0 mg/L DS, and 0 or 5 mmol/L DBS (Fig. 1a) when compared with those under low pH. This increase was larger for the solutions with 10 mmol/L NaCl, indicating that NaCl influenced the 222.5 nm UV absorbance. However, for the solutions of 0.1 mmol/L NaCl, the difference in the absorbance at 222.5 nm between the different pH values decreased with increasing DBS and DS concentrations (Fig. 1a). The influence of the electrolyte was restricted by the addition of DOM and DBS to solutions containing a smaller concentration of NaCl. Because of this restriction by DBS, an increase in the slope of the regression line, in DS concentration vs. 222.5 nm absorbance, was observed

with the increase in DBS concentration under high pH (Fig. 1a). For 10 mmol/L NaCl solution, the 222.5 nm absorbance was always larger under the higher pH, and no significant influence of DBS and DS was noticed with the change in pH (Fig. 1b). Such stronger pH influence was considered to be due to the higher NaCl concentration and the lower DS concentration in the 10 mmol/L NaCl solution. Similar findings for higher NaCl concentration with a lower DOM quantity have been reported by Noto & Mecozzi (1997).

However, for the 0 mg/L DS solution, no significant influence of pH on the absorbance in the 400 nm UV-vis spectrum was observed (Fig. 2). The DS-free electrolyte solution of NaCl did not affect the 400 nm UV-vis absorbance because the 0 mg/L DS solution was transparent. However, the difference between the absorbance at different pH values increased with increasing DOM concentration (Fig. 2). It is presumed that the turbidity of the solution decreased under higher pH conditions through the conformational change in DOM, which ultimately decreased the UV-vis absorbance at 400 nm. Under elevated pH, the DOM swelled due to the increase in electrostatic repulsive force among the negative electric charges on its surface, which increased with the increase in pH. The swelling of DOM enhanced the expansion of humic and fulvic coils, which ultimately increased the transparency of the DBS–DOM solution and caused a decrease in UV-vis absorbance. Klucáková (2018), de Melo et al. (2016), and Ghosh and Schnitzer (1980) stated that the phenolic and carboxylic groups of humic acid and fulvic acid are deprotonated in alkaline conditions, and the repulsion of these negatively charged groups cause the expansion of humic and fulvic coils and the liberation of small particles from them. This phenomenon may be responsible for the above-mentioned changes in the absorbance characteristics of the studied DBS–DOM complex solutions.

The pH-induced differences in the 400 nm absorbance between the same DS values decreased as the DBS concentration increased in the DBS–DOM solution with 0.1 mmol/L NaCl (Fig. 2a). DBS is thought to interact with DOM and affect the transparency of the solution.

When DBS is added, DBS might decrease the space where DOM can move freely due to the negative charge of DBS. This type of restriction may decrease the transparency and increase the absorbance of the DBS–DOM solution under spectrometry. Therefore, the difference between the different pH values with similar DS concentrations became smaller. However, the combined influence of pH and added DBS concentration was not clear for the DBS–DOM complex solution with 10 mmol/L NaCl. This obscurity is most likely because the DOM concentration was too small to interact with DBS and the absorbance difference was negligible.

The comparison between the 222.5 nm UV and 400 nm UV-vis spectra showed a decent linear relationship for the DBS–DOM complex solution with different concentrations of DS, DBS, and electrolytes under the lower (5.5 and 6.5) and higher (12.5) pH conditions (Fig. 3). The clear difference in the influence of pH on both absorbances is exhibited in Figure 3, where it can be observed that the absorbance at 222.5 nm increased and the absorbance at 400 nm decreased with increasing pH. This is thought to have occurred due to the previously mentioned influences of NaCl and structural changes in DOM. This indicates that the absorbance at 400 nm in the UV-vis spectrum more accurately represents the DOM species in the solution rather than the DS concentration. Therefore, the use of a linear regression model (Hossain and Ishiguro 2021) to remove the influence of DOM should also be equally efficient under the higher pH conditions of the DBS–DOM complex solution. Consequently, as shown in Figures 5 and 6, the preciseness of the measurement of DBS from the DBS–DOM complex solution using the newly developed UV spectrometric method, under both lower and higher pH conditions, was deemed suitable for practical applications.

CONCLUSION

The efficacy of the photometric method for the precise estimation of DBS at higher pH conditions was assessed in this study through comparisons with the already recognized use of this method under low pH conditions. Because the conformational change in DOM occurred under alkaline conditions, validating this newly developed method under conditions of higher pH is a timely accomplishment. Although the conformational change in DOM occurred under a strong alkaline condition, which further influenced the absorbance characteristics of the DBS–DOM aqueous solution, the effect of DOM observed in conventional UV spectrometry was successfully avoided using this new approach. Hence, the efficacy of the studied photometric method was evidenced even under strong alkaline conditions for the DBS–DOM complex solution with a substantial quantity of DOM. Future research opportunities have been opened for this analysis to aid in exploring the mechanism of combined interaction within the DBS–DOM–NaOH solution at the ultra-microscopic and molecular levels. Additional justification for this reagent-less, inexpensive, quick, and environmentally friendly method can be further validated using various DBS–DOM complex solutions with a moderately alkaline pH (~8.0) range.

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AUTHOR CONTRIBUTIONS

Md. Imam Hossain: Methodology, Investigation, Formal analysis, Validation, Writing - original draft, Writing-review & editing.

Munehide Ishiguro: Methodology, Investigation, Validation, Writing-review & editing, Supervision, Funding acquisition.

Both authors contributed to and approved the final draft of the manuscript.

ETHICS STATEMENT

No human or animal specimen was used in the experimentation of this research and institutional ethical approval was not required.

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565 **Table 1:** The coefficient of determination (R^2) and slopes from the regression analyses between
566 the dissolved solids (DS) concentration and the absorbances and between the absorbances for
567 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions having lower (pH 6.5 and pH 5.5) and higher
568 pH (12.5) condition.

Regression between		0.1 mmol NaCl/L		10 mmol NaCl/L	
		pH 6.5	pH 12.5	pH 5.5	pH 12.5
DS conc. vs. Abs. at 222.5 nm	R^2	0.962–0.967	0.960–0.976	0.605–0.870	0.666–0.917
	Slope	0.017–0.018	0.015–0.017	0.0039–0.0045	0.0038–0.0045
DS conc. vs. Abs. at 400 nm	R^2	0.980–0.982	0.964–0.979	0.790–0.816	0.652–0.862
	Slope	0.0032	0.0025–0.0028	0.00055–0.00057	0.00020–0.00022
Abs. at 222.5 nm vs. Abs. at 400 nm	R^2	0.990–0.994	0.998-0.999	0.0776–0.981	0.747–0.926
	Slope	5.5–5.6	6.0–6.2	7.2–7.7	16–18

569 * R^2 and slope range (Min.–Max.)

570

571 **FIGURE CAPTIONS**

572

573 **Figure 1**: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations
574 on the 222.5 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)**
575 10 mmol NaCl/L solutions.

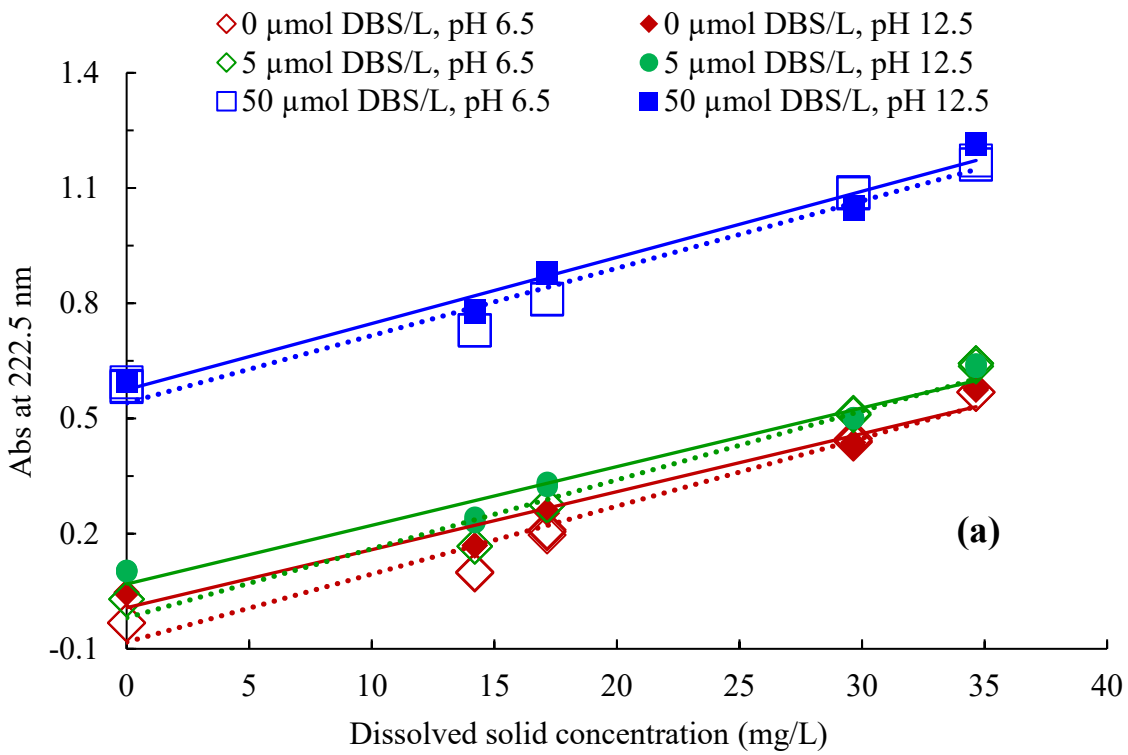
576 **Figure 2**: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations
577 on the 400 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10
578 mmol NaCl/L solutions.

579 **Figure 3**: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra
580 measured with respect to the dodecylbenzenesulfonate (DBS) concentration at low and high
581 pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.

582 **Figure 4**: Relationship between the actual and measured dodecylbenzenesulfonate (DBS)
583 concentrations for DBS–DOM complex solutions **at pH 12.5** with **(a)** 0.1 mmol NaCl/L and
584 **(b)** 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The
585 dotted line is the standard DBS curve.

586 **Figure 5**: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the
587 respective actual values for the DBS–DOM complex solutions **at pH 12.5** with **(a)** 0.1 mmol
588 NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS).
589 The dotted line is the standard DBS curve.

590



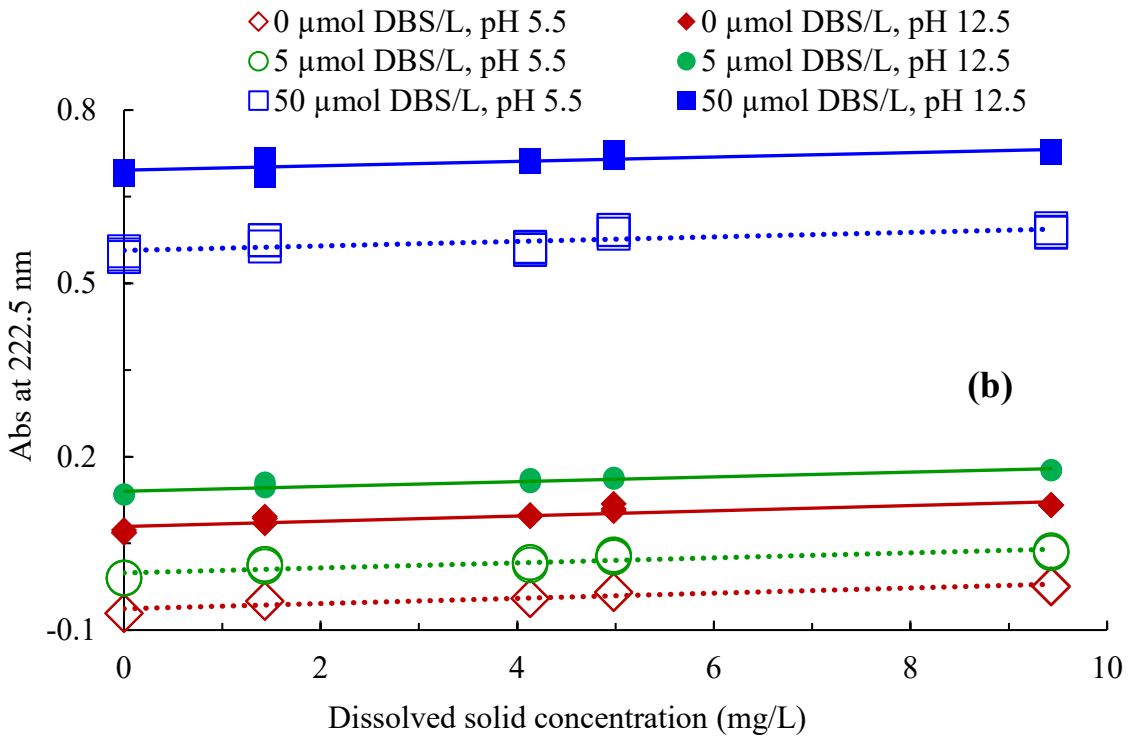
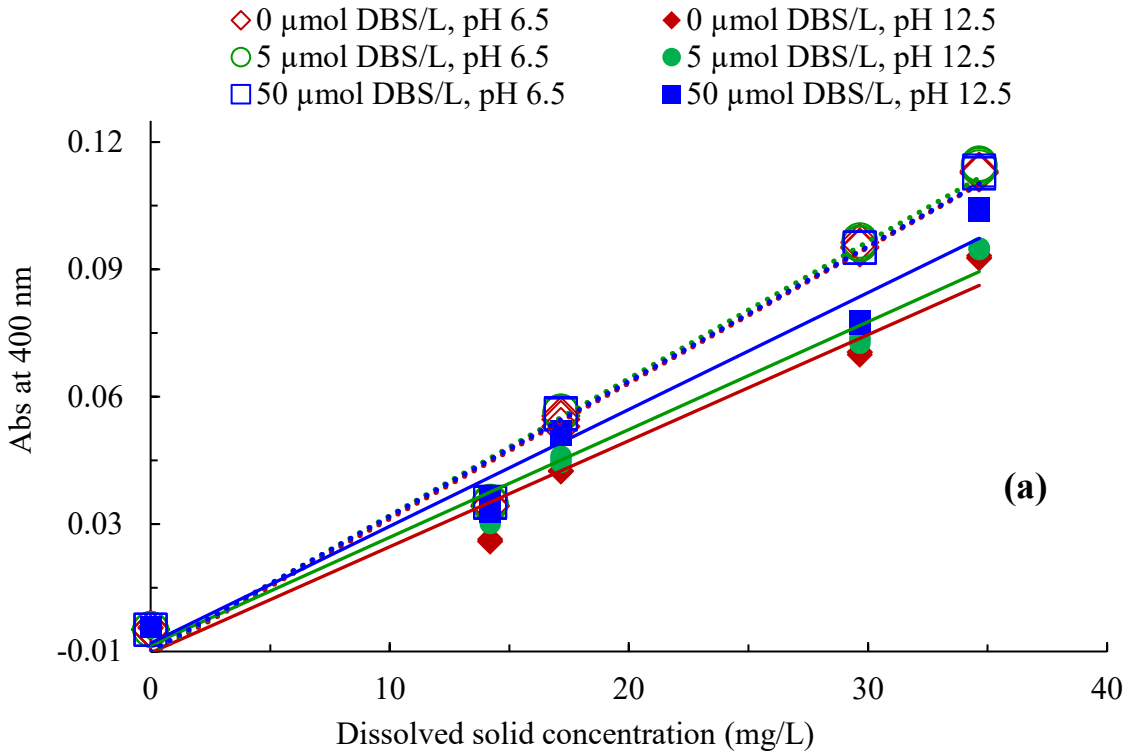


Figure 1: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 222.5 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.



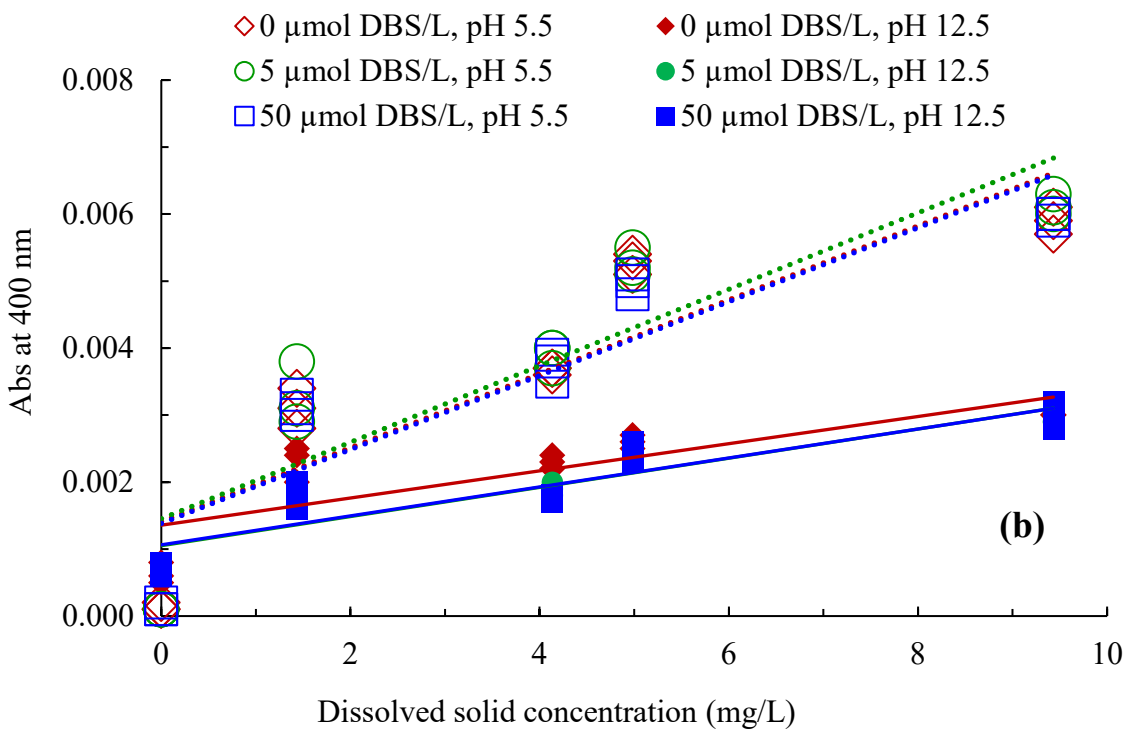
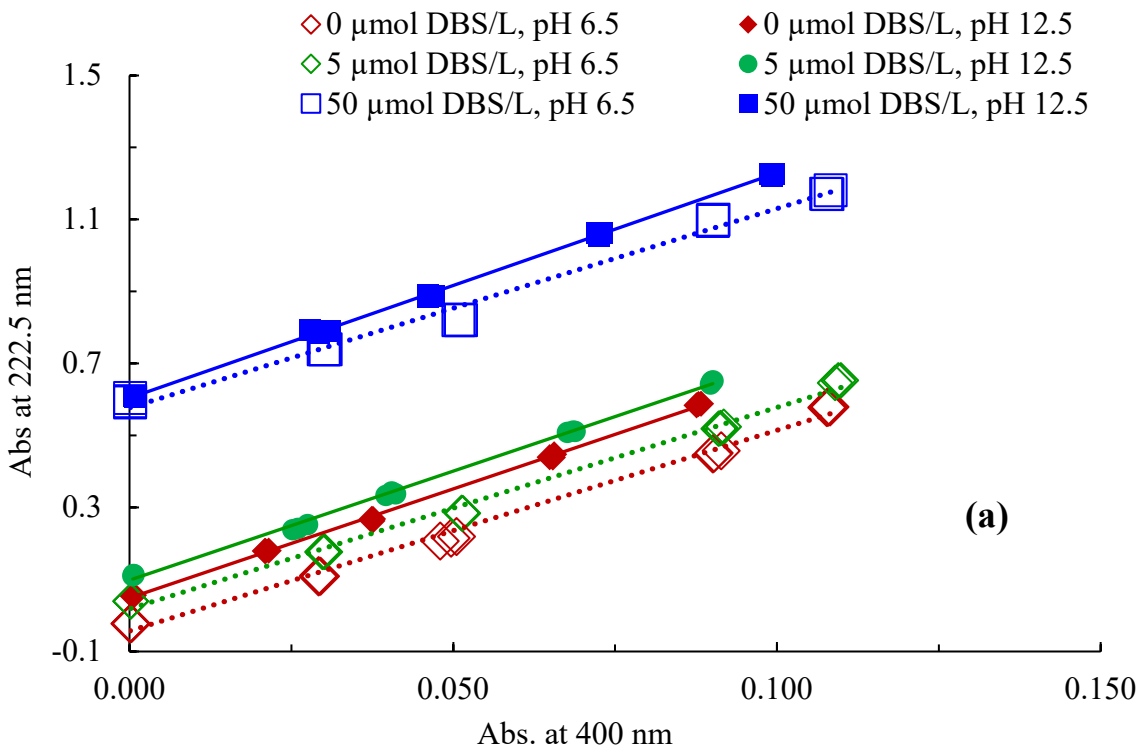


Figure 2: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 400 nm spectrum at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.



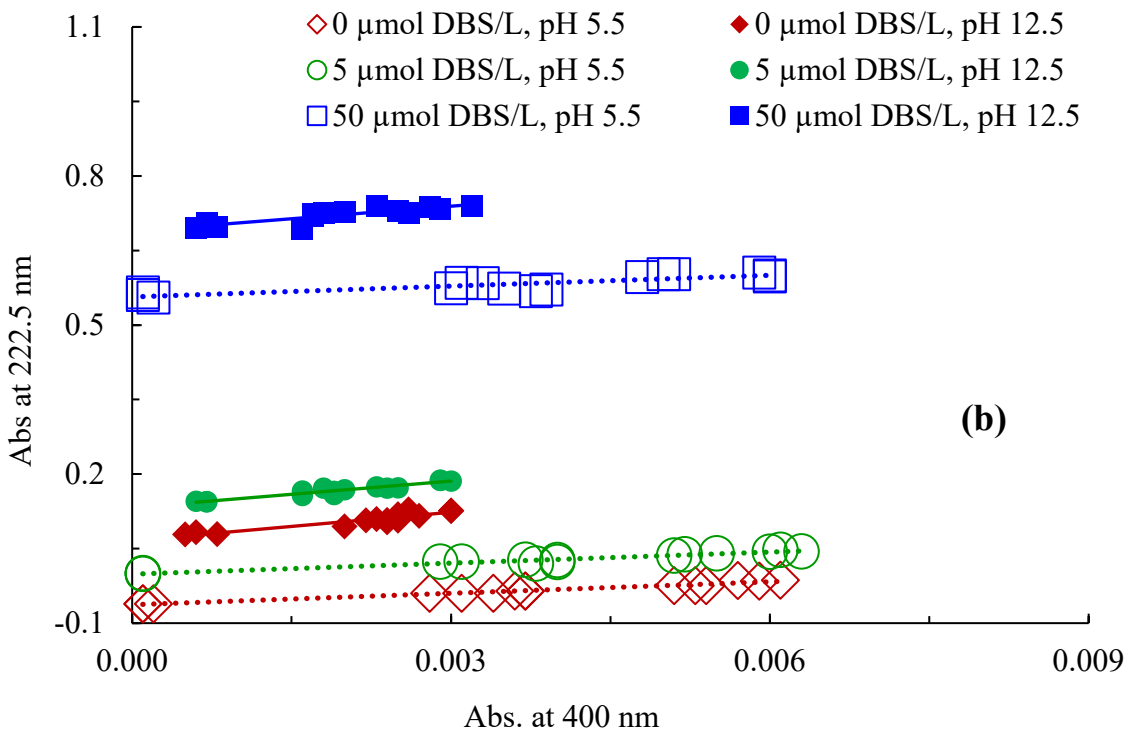
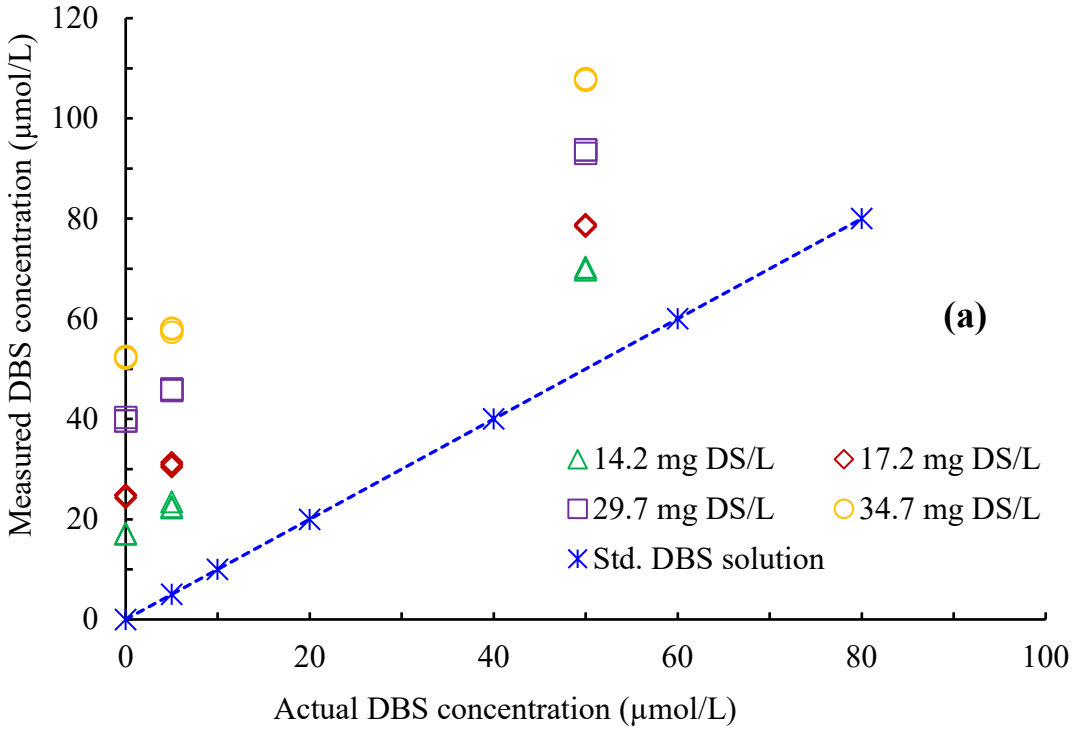


Figure 3: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra measured with respect to the dodecylbenzenesulfonate (DBS) concentration at low and high pH condition for the **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L solutions.



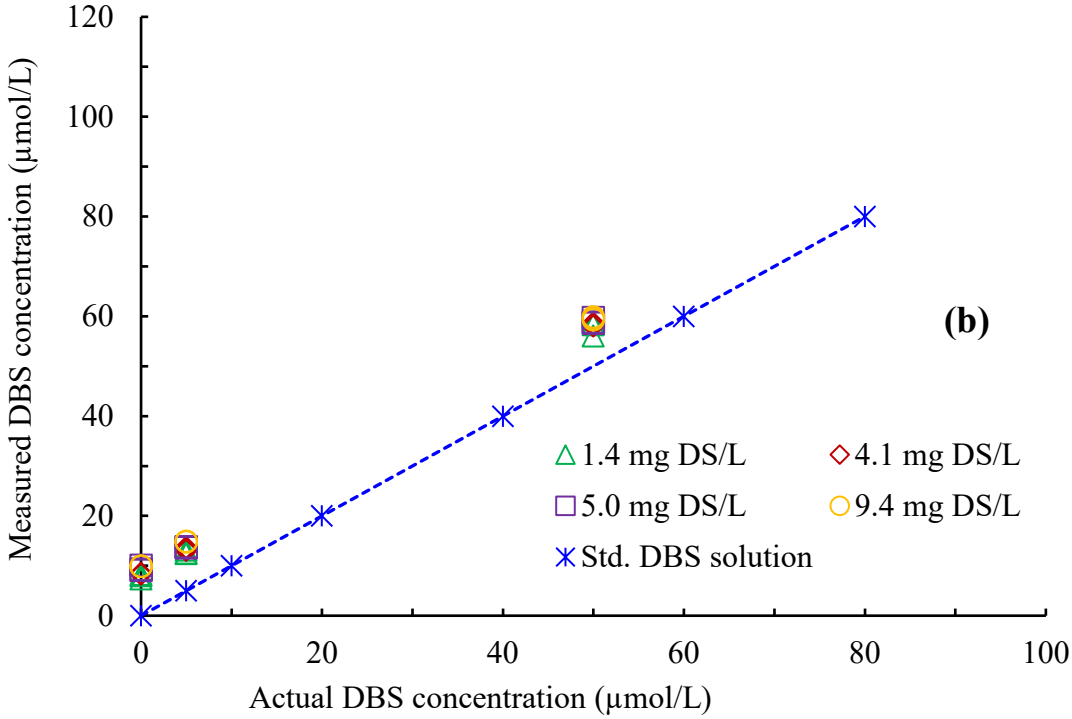
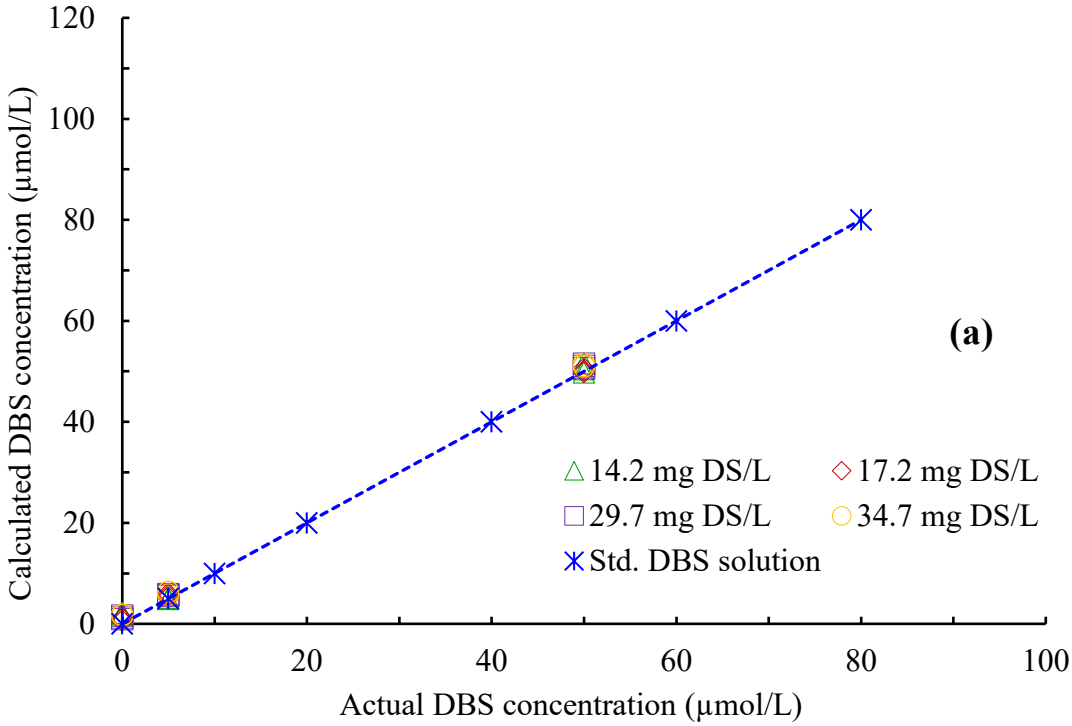


Figure 4: Relationship between the actual and measured dodecylbenzenesulfonate (DBS) concentrations for DBS–DOM complex solutions at pH 12.5 with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.



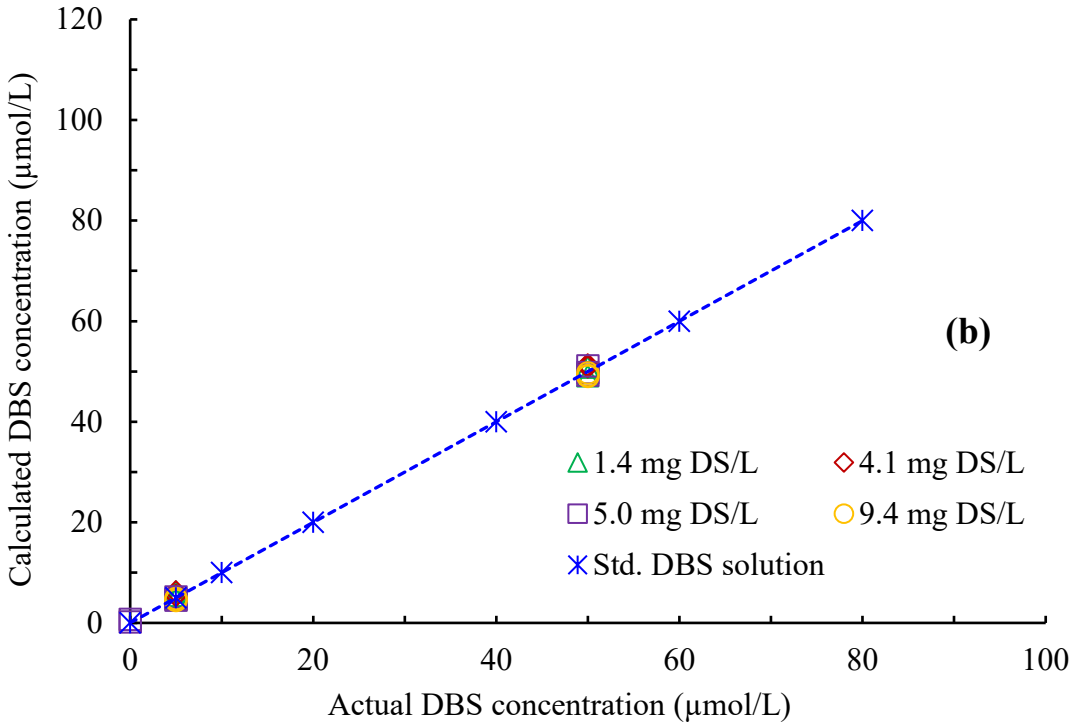


Figure 5: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the respective actual values for the DBS–DOM complex solutions at pH 12.5 with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.