AGGREGATIONAL ATTITUDE OF HEXADECYLTRIMETHYLAMMONIUM BROMIDE AQUEOUS SOLUTIONS OF SODIUM SALT AT 298.15K

Osundiya Olubunmi Medinat† --- Olaseni Segun Esan‡
†Department of Chemistry, Lagos State University Ojo, Lagos, Nigeria
‡Department of Chemical Sciences, Adekunle Ajasin University, Akungba, Akoko, Nigeria

ABSTRACT

This research reports micelle formation of hexadecyltrimethylammonium bromide and the dependence of aggregation number on the array of sodium salts in aqueous solution. Critical micelle concentration, degree of micelle ionization, and aggregation number were obtained from electrical conductivity measurement. Pseudo-phase separation model was used to evaluate and discussed standard Gibb’s free energy of micellization. It was observed that hexadecyltrimethylammonium bromide critical micelle concentration decreases while aggregation number increases. Amongst the sodium salt, disodium hydrogen phosphate was found to have the highest tendency in reducing hexadecyltrimethylammonium bromide critical micelle concentration. The sodium salts with the highest valency anion strongly promote micellization of hexadecyltrimethylammonium bromide, indicating the dependence of aggregation phenomenon on the availability of anion.

Keywords: Aggregation number, Micellization, Hexadecyltrimethylammonium bromide, Valency, CMC, Sodium salt.

1. INTRODUCTION

Solubilization of chemical species in micelles is as a function of properties of the chemical, the micelle, the kind of interactions, plus the ability to interaction with the micelle [1]. Aggregational attitude of ionic surfactant in solution has been ascribed to two opposing phenomena: a promotional effect involving the removal of the non-polar mostly hydrocarbon from the aqueous environment, and repulsions among head groups resulting in demotional effect [2-5]. Though repulsions among ionic head groups are reasonably control by the association of counter-ions to the micelle surface. Formation of aggregates, CMC, micellar size and shape are control by the physicochemical regulations between the two processes and the counter-ions. Availability of electrolytes in ionic surfactant solution causes depression of the CMC though counter-ions influence the shape and size depending on the characteristic of the counter-ions [2]. Functionality of electrolyte ion can be arranged either as salting in or silting out agent. This arrangement control major role in a lot of activity like in biological and physicochemical processes, namely; aggregation of amphiphile, surface tension of electrolyte, cloud point of surfactant and polymer [4].

© 2016 Conscientia Beam. All Rights Reserved
Many researchers have monitored the effect of salts on micellization in line with lyotropic series \[6\]. Though it has been a long time suggestion on the equilibrium of Hofmeister sols and dissolution of proteins in electrolyte solutions \[2\]. The Hofmeister series can be categorized either as water structure maker (kosmotropic) or water structure breaker (chaotropic) \[7\]. At the interface of micelles, kosmotropic helps in building water structure which is broken by chaotropic \[7\]. At the interface of micelles, kosmotropic helps in building water structure which is broken by chaotropic \[7\]. Large hydrated radii accompanying with small polarizability and weaker electrostatic interaction are general characteristic of kosmotropic. It was suggested that up to the micellar surface, small ion does not show specificity in binding to aggregated monomer (micelle) as well as retaining their mobility and water of hydration inclusive \[8\]. The chaotropes are accompanying with the following characteristic: (i) large radii (ii) enough polarizability, (iii) weak electrostatic interaction and ability to lose their water of hydration easily. Elucidation from NMR data suggested that they were involved in ion-pairing. Researcher has elaborately examined the Hofmeister or lyotropic effects on various physicochemical properties and parameters from which importance and versatility of the series can be confirmed \[9-11\].

In aqueous solution, availability of electrolytes causes depression in CMC of most surfactants, with the greatest effect being found for ionic surfactants \[11-15\]. Investigation has shown that inorganic salt has a significant effect on the adsorption of ionic surfactant in air/water interface including their aggregation in aqueous media. This is because the salt in this case decreases the thickness of the ionic atmosphere surrounding the ionic head groups and consequently decreased electrical repulsion between the head group within the adsorption film and the micelle \[14-16\]. The addition of a wide variety of inorganic salts leads to rearrangement of micellar shape and gives wide variation in the catalytic ability of the aggregated monomers (i.e micelle).

Uncountable information on the addition of electrolyte to surfactant solution has been documented \[17-19\] yet their mechanism at molecular level remains unclear. In this work, a systematic study on the conductometric properties of aqueous solutions of a model cationic surfactant, HTABr, was performed in the absence and presence of series of electrolytes. This was done to obtain further evidence on the Hofmeister effects produced by the addition of different electrolytes to aqueous solutions of surfactants. The result obtained from this study shall help to make a thorough elucidation of the Hofmeister effects of anions likewise the role of hydrophobic properties of the electrolytes on the micellization of HTABr in aqueous media. In this study, five sodium electrolytes (NaCl, Na₂HPO₄, Na₂CO₃, Na₂SO₄, and NaNO₃) were used, and in the absence and presence of 1mM of sodium salt, conductivity value of HTABr solutions were taken.

2. MATERIALS AND METHOD

2.1. Chemicals

List of chemical used and their properties in this research were listed in Table 1. The entire chemicals were used as obtained. Double-distilled and deionized water was used.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>NaNO₃</th>
<th>Na₂HPO₄</th>
<th>NaCl</th>
<th>Na₂CO₃</th>
<th>Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>source</td>
<td>Sinopharm chemical Reagent Corp</td>
<td>Sinopharm chemical Reagent Corp</td>
<td>Sinopharm chemical Reagent Corp</td>
<td>Sinopharm chemical Reagent Corp</td>
<td>Sinopharm chemical Reagent Corp</td>
</tr>
<tr>
<td>% purity</td>
<td>98.5</td>
<td>99.4</td>
<td>98.5</td>
<td>98.5</td>
<td>99.5</td>
</tr>
</tbody>
</table>

2.2. Conductivity Measurements

The conductivity measurements were taken using a Jenway Conductivity Bridge of certainty (±0.02 µScm⁻¹). The conductivity bridge was calibrated by the determination of cell constant, \(K_{cell}\), using different standard KCl solutions, whose concentration were known and known specific conductance, \(k\), at room temperature (298.15K) \[11\]. Temperature was adjusted within an accuracy of ±0.1 K, of a desired temperature using an automatic
thermostat bath (from Medica Mgf. Co, India). Conductivity Bridge under calibration were used to measure the conductivity value of these solution. The cell constant is the ratio of the known specific conductance of the standard KCl solutions and the measured specific conductance of the same solution at 298.15 K. The calculated cell constant was then compared with the cell constant value provided with the conductivity cell. If there was any difference between the cell constant values, the conductivity bridge was adjusted to the determined cell constant value.

Conductivity values were taken at different concentrations of HTABr. To prevent dilution error in the preparation of different HTABr solution, the concentration of the sample solution was successively increased by a stepwise addition of 0.20mL of HTABr in salts solution to 20.0 mL of salt solution, then titration of addition of HTABr is continue. After each successive increment, the solutions were subjected to a homogeneous mixing before taken the conductivity value. The conductivity was taken in duplicate on the average value of the measurement.

3. RESULTS AND DISCUSSION

3.1. Determination of CMC and Degree of Ionization (B)

Electrical conductivity is a sensitive, simple and reliable technique for the detection of CMC. The conductivity of amphiphilic solution undergoes abrupt change at CMC. The electrical conductivity, k, measured at room temperature (298.15 K) was carried out to obtain information about the Hofmeister effect that is produced by the addition of different electrolytes to aqueous solution of HTABr. The values of conductivity of the micelled solution of HTABr, with and without sodium salts, at room temperature (298.15 K) are presented in Fig 1. The two straight line plots, having different slope, intersect at point that corresponded to the CMC value. Below the CMC value, the increasing conductivity with concentration, which is generally observed for dilute solutions, was attributed to the increasing number of free HTA\(^+\) and Br\(^-\) ions in solution, whereas the small increase in the conductivity values above the CMC was attributed to two factors: (i) attraction of parts of counter-ions directly to micellar surface which resulted in effective loss of ionic charges making the counter-ions become dynamic part of the aggregated micelle which promote high surface charge and reducing the available ion carrier, (ii) the aggregated micelle contribute to the conductance better than the free ion that is less mobile \[20\].

![Fig-1. Plot of the conductivity (k) versus [HTABr] in aqueous media of different sodium electrolytes at 298.15K.](image)

The result presented in Table 2 showed that the CMC value of HTABr decreased with the addition of sodium salts, which is an indication that, the significant role of electrolytes in the micellization process, which is a characteristic behaviour of an ionic surfactant, is due to the layer formed at the air-solution interface \[21-23\].

Addition of electrolytes is known to reduce the thickness of the ionic atmosphere surrounding the ionic head groups between opposite charges which facilitate uptake of surfactant ions \[24-28\]. For the same cation (i.e Na\(^+\)),
the effect of anions in lowering of the CMC values of HTABr followed the Hoffmeister series, for the strength of the salt effects of electrolyte; NaCl > NaNO₃ > Na₂CO₃ > Na₂SO₄ > NaH₂PO₄. This indicated that anions with higher charge (which are called structure-making ions, since they induce a more coherent structure of the water) are more effective than anions with lower valence in the aggregation process. This observation was due to effective coulombic interaction between oppositely charge surfactant head groups and electrolyte plus decrease in electrostatic repulsion between the charged head groups [29]. Theoretical prediction shows (Figure 2) that HTABr surfactant interacts strongly with sodium salts, where part of the counter-ions that are released by the surfactant heads and by the added electrolytes remain within the stern layer of the micelles as bound counterions on the micelle surface. The counterions that remained bound to to the surface of micelle are distributed among the HTABr heads, causing a lowering of the net micelle charge surface and the electrostatic repulsion, generated by the charged HTABr micelle.

As shown in Figure 1, the ability of the investigated anion to increase K value, i.e conductivity of the solvent which is the specific conductivity of the solvent followed the sequence Na₂CO₃ > Na₂SO₄ > NaNO₃ > NaCl > NaH₂PO₄. This correlation specific effect, with the series of Hofmeister anion, was attributed to the hydrophobic nature of the anions. Above the CMC value, due to the penetration of hydrophobic portion of the sodium salt into the aggregated micelle, and charge neutralization, anions hydrophobicity may stimulate change in structure and increased the sizes of the micelle.

This would definitely have strong effect in lowering the value of the conductivity of HTABr in aqueous media. As presented in Figure 1, the shape of the plot of K versus HTABr concentration in the presence of sodium salt is similar to that found in pure aqueous solutions. This suggested that there was no more of X⁻ available to induce the formulation of X⁻/HTABr⁺ aggregates, and consequently, HTABr will be in excess and will behave in a similar way to that occurring without sodium salt.

The following relation was derived from conductivity measurement [29] for the estimation of degree of ionization (β)

\[ \beta = 1 - \frac{S_2}{S_1} \]  \hspace{1cm} (1)

The observed values of β for HTABr solution (Table 2) was 0.74 at 298.15 K, which compared well with the corresponding literature value of 0.74 [30]. Na₃HPO₄ had the largest β and smallest CMC value (Table 2). This was attributed to the fact that this anion has a hydrophobic fragment and can be solubilized in the interior of the
micelles, which acted as a hydrophobic environment. The stronger anionic bonding resulted in the depression of the electrostatic repulsion between the head groups of the surfactant, large decrease in the CMC values and the higher aggregation number of the corresponding micelles.

The CMC values of the investigated anions decreased in the order Na$_2$HPO$_4$ < Na$_2$CO$_3$ < Na$_2$SO$_4$ < NaNO$_3$ < NaCl, while the β values were in the reversed order. The results presented in Table 2 showed that all salts studied reduced CMC values of HTABr and the higher the valency of anions, the faster it promoted micellization of HTABr. This was attributed to electrostatic association of the added salt anion with cation head group of HTABr which lead to the reduction in electrostatic repulsion among HTABr head groups.

Reports has shown that [2, 31] counter-ions with large size bind more effectively to micelle surface which promote decrease in electrostatic repulsion between the head groups of surfactant, thereby increase surfactant aggregational tendency resulting into depression of its CMC value. Addition of salt to aqueous media of HTABr lead to the partial reduction of the water of hydrophobic hydration around the alkyl chain of the non-associated surfactant monomers which decreased the energy required to break down this structure during micellization process [18]. This also led to easier formation of micelles (lowering of the CMC value). Anions with higher valency hydrated more water molecule and therefore they are more effective than anions with lower valency to promote the surfactant to go to micellar phase (pseudo phase) similar to the one observed in the case of aqueous two-phase system formulation [32, 33].

The CMC values of the investigated anions decreased in the order Na$_2$HPO$_4$ < Na$_2$CO$_3$ < Na$_2$SO$_4$ < NaNO$_3$ < NaCl, while the β values were in the reversed order. The results presented in Table 2 showed that all salts studied reduced CMC values of HTABr and the higher the valency of anions, the faster it promoted micellization of HTABr. This was attributed to electrostatic association of the added salt anion with cation head group of HTABr which lead to the reduction in electrostatic repulsion among HTABr head groups.

Reports has shown that [2, 31] counter-ions with large size bind more effectively to micelle surface which promote decrease in electrostatic repulsion between the head groups of surfactant, thereby increase surfactant aggregational tendency resulting into depression of its CMC value. Addition of salt to aqueous media of HTABr lead to the partial reduction of the water of hydrophobic hydration around the alkyl chain of the non-associated surfactant monomers which decreased the energy required to break down this structure during micellization process [18]. This also led to easier formation of micelles (lowering of the CMC value). Anions with higher valency hydrated more water molecule and therefore they are more effective than anions with lower valency to promote the surfactant to go to micellar phase (pseudo phase) similar to the one observed in the case of aqueous two-phase system formulation [32, 33].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Zero Salt</th>
<th>NaCl</th>
<th>Na$_2$HPO$_4$</th>
<th>NaNO$_3$</th>
<th>Na$_2$SO$_4$</th>
<th>Na$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>0.96</td>
<td>0.71</td>
<td>0.05</td>
<td>0.52</td>
<td>0.38</td>
<td>0.24</td>
</tr>
<tr>
<td>β</td>
<td>0.74</td>
<td>0.64</td>
<td>0.79</td>
<td>0.68</td>
<td>0.73</td>
<td>0.75</td>
</tr>
<tr>
<td>n</td>
<td>55</td>
<td>58</td>
<td>72</td>
<td>61</td>
<td>69</td>
<td>65</td>
</tr>
</tbody>
</table>

Using pseudo-phase separation model, the standard Gibbs free energy of micellization in aqueous salt solution was obtained from the relation

\[
\Delta G^o_{mic} = RT[\ln x_{cmc} + \beta \ln(X_s + x_{cmc})]
\]

where \(x_{cmc}\) is the mole fraction of the surfactant at CMC, and \(X_s\) is the mole fraction of the electrolytes. The values of \(\Delta G^o_{mic}\) for the investigated system were negative and they were in the order HPO$_4^{2-}$ (-38.436KJ/mol) > SO$_4^{2-}$ (-35.128KJ/mol) > NO$_3^-$ (-34.614KJ/mol) > CO$_3^{2-}$ (-33.996KJ/mol) > Cl$^-$ (-31.411KJ/mol), which shows that aggregation of monomer to form micelles in the presence of large sized counter-ions is more spontaneous than those with the availability of small size counter ions as reported for dodecyltrimethylammonium bromide a cationic surfactant in the literature [19].

The conductivity data, obtained for HTABr solution at lower concentration range was used to estimate, by extrapolation, the equivalent conductivity of the solvent at infinite dilution, \(\Lambda_0\). An estimation of the micellar charge from conductivity data of aqueous surfactant solutions was made by applying the approach of Kimizuka and Satake [34]. They assumed that at above the CMC value, only one kind of micelle aggregation number (n), with a counterion amounting to β. An additional assumption that \(\Lambda = \Lambda_0 + a \sqrt{I}\), where \(a\) is a constant and \(I\) the ionic strength, is valid in the pre- and post micellar regions and lead to the equation

\[
\left(\frac{\Lambda_0 - \Lambda}{\Lambda_0 - \Lambda_{cmc}}\right)^2 = 1 - \frac{\beta(1+n\beta)}{2} + \frac{\beta(1+n\beta)}{2} \left(\frac{C}{C_{cmc}}\right)
\]
Where $\Lambda_{\text{cmc}}$ is the equivalent conductivity of the solution just at the CMC from the linear relation between
\[
\left(\frac{\Lambda_0 - \Lambda}{\Lambda_0 - \Lambda_{\text{cmc}}}\right)^2 \text{ and } \frac{C}{C_{\text{cmc}}},
\]
the value of aggregation number $n$ can be inferred. The value of $H$ can be estimated either from intercept or from slope of equation 3. Both approaches yielded values of $n$.

4. CONCLUSIONS
HTABr surfactant interacted strongly with sodium salts, where parts of the counter-ions released by the surfactant heads and the added electrolytes remained within the stern layer of the micelles as bounded counter-ions on the surface of micelle. Counter-ions that remained bound to the surface of micelle were distributed among the HTABr heads. This caused the lowering of the net micelle surface charge and the electrostatic repulsion generated by the charged HTABr micelle. The evaluation of the obtained CMC of HTABr showed the existence of strong electrostatic interactions with the sodium salt, resulting in the partial reduction of water of hydrophobic hydration of non-aggregated surfactant monomers. These further decreased the energy needed to break down the structure of HTABr, leading to easier formation of micelle. Higher value of CMC of HTABr in the presence of NaNO$_3$, NaCl, Na$_2$CO$_3$, and Na$_2$SO$_4$ showed the availability of more of these salts in solution which are not interacting with HTABr surfactant molecule. Negative value of $\Delta G_m^0$ further affirmed the spontaneity of the interaction.

Funding: This study received no specific financial support.
Competing Interests: The authors declare that they have no competing interests.
Contributors/Acknowledgement: All authors contributed equally to the conception and design of the study.

REFERENCES


