EFFECT OF MIXED MICELLES ON RELATIVE COUNTERION BINDING CONSTANTS AND COUNTERION-INDUCED MICELLAR GROWTH

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EFFECT OF MIXED MICELLES ON RELATIVE COUNTERION BINDING CONSTANTS AND COUNTERION-INDUCED MICELLAR GROWTH

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ABSTRACT

Semi empirical kinetic technique has been used to determine the values of both cationic CTABr (hexadecyltrimethylammonium bromide) and mixed cationic-nonionic CTABr-C_{16}E_{20} (hexadecyltrimethylammonium bromide-polyethoxy hexadecyl ether) micellar relative binding constants ($K_X$/K_{Br} and $^mK_X$/K_{Br}) of counterions, X\textsuperscript{−} and Br\textsuperscript{−}, (= K^{Br}_X or R^{Br}_X and $^mK^{Br}_X$ or $^mR^{Br}_X$), where superscript “m” signifies mixed micellar system, for X\textsuperscript{−} = 2-NaOC_{6}H_{4}CO\textsuperscript{2−}, 3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−} and 4-ClC_{6}H_{4}CO\textsuperscript{2−} and correlate them to their specific rheological observations. The kinetic investigations on the influence of CTABr-C_{16}E_{20} on the values of $K^{XBr}$ or $^mK^{XBr}$ in aqueous solutions of 2-NaOC_{6}H_{4}CO\textsuperscript{2−}Na and NaBr has been carried out. The presence of 0.006 M C_{16}E_{20} decreases the mean values of $K^{XBr}$ or $^mK^{XBr}$ from 42 to 16 (2.6-fold lower). Rheological measurements of 0.015 M CTABr/2-NaOC_{6}H_{4}CO\textsuperscript{2−}Na/H_{2}O solutions at 25 and 35 °C revealed a single maximum for [2-NaOC_{6}H_{4}CO\textsuperscript{2−}Na] = 0.02 M as the zero shear viscosity ($\eta_o$) was plotted against [2-NaOC_{6}H_{4}CO\textsuperscript{2−}Na]. This shows, indirectly, that the is a possibility of the presence of wormlike micelles whereas the possible existence of spherical micelles was revealed at [C_{16}E_{20}] ≥ 0.006 M. A similar study, with a different counterion, 3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−} has also been reported. The average value of $K^{Br}_X$ or $R^{Br}_X$, for CTABr/3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na/H_{2}O solution ($K^{Br}_X$ or $R^{Br}_X = 198$) appeared to be almost 2½-fold larger than that of CTABr/3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na/C_{16}E_{20}/H_{2}O ($^mK^{Br}_X$ or $^mR^{Br}_X = 78$). Rheometric results of 0.015 M CTABr/3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na/H_{2}O solution at 25 and 35 °C indicate that the plot of zero shear viscosity ($\eta_o$) against [3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na] has two maxima at two different concentrations of 3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na (0.015 and 0.04 M) and this also shows the possible existence of wormlike micelles. Contrarily, a possible formation of spherical micelles for CTABr/3,5-Cl_{2}C_{6}H_{3}CO\textsuperscript{2−}Na/C_{16}E_{20}/H_{2}O solution ([CTABr]_{T} = 0.015 M and [C_{16}E_{20}]_{T} = 0.006 M) was observed at the same temperatures. The effects of CTABr-C_{16}E_{20} on 4-
ClC₆H₄CO₂⁻ has also been investigated. The respective mean values of KₓBr or RₓBr obtained for CTABr/4-ClC₆H₄CO₂Na/H₂O solution (KₓBr or RₓBr = 50) is 2.3-fold larger than that of CTABr/4-ClC₆H₄CO₂Na/C₁₆E₂₀/H₂O (mKₓBr or mRₓBr = 22). The possible existence of wormlike micelles was also observed from the rheometric data of 0.015 M CTABr/4-ClC₆H₄CO₂Na/H₂O solution based on the plot of η₀ against [4-ClC₆H₄CO₂Na]. The observation also revealed the presence of a single maximum at [4-ClC₆H₄CO₂Na] = 0.03 M where it was thought that spherical micelles were formed in CTABr/4-ClC₆H₄CO₂Na/C₁₆E₂₀/H₂O with 0.015 M CTABr and 0.006 M C₁₆E₂₀. The quantitative correlation between the magnitudes of relative countorion (X⁻) binding constant (KₓBr or RₓBr and mKₓBr or mRₓBr) and X⁻-induced cationic micellar structural growth have been reported for the first time in this thesis. The highlight on the possible cause was that adding nonionic surfactant to an aqueous solution of cationic micelle-forming surfactant could be a technique to achieving changes in the structural, as well as the viscoelastic behavior of cationic micelles in the presence of certain inert organic salts.
ABSTRAK

Teknik kinetik separa empirik telah digunakan untuk menentukan nilai relatif pemalar ikatan misel untuk kedua-dua bahan kation CTABr (heksadecytrimethylammonium bromida) dan campuran bahan kation-bukan kation CTABr-C16E20 (hexadecytrimethylammonium bromide-polietoksik heksadecil ether) (K_X/K_Br and mK_X/mK_Br) dengan ion-lawan X^- dan Br^- (= K_X^Br or R_X^Br and mK_X^Br or mR_X^Br), di mana superskrip "m" menandakan sistem campuran misel, untuk X^- = 2-NaOC_6H_4CO_2^-, 3,5-Cl_2C_6H_4CO_2^- dan 4-ClC_6H_4CO_2^- dan mengaitkannya dengan pemerhatian rheologinya secara khusus. Penyiasatan kinetik mengenai pengaruh CTABr-C16E20 terhadap nilai-nilai K_X^Br atau R_X^Br dalam larutan akueus 2-NaOC_6H_4CO_2Na dan NaBr telah dilaksanakan. Kehadiran 0.006 M M C16E20 menurunkan nilai min K_X^Br atau R_X^Br dari 42 ke 16 (2.6-kali lebih rendah). Pengukuran rheologi 0.015 M CTABr/2-NaOC_6H_4CO_2Na/H_2O pada 25 °C dan 35 °C menunjukkan satu maksimum tunggal untuk [2-NaOC_6H_4CO_2Na] = 0.02 M apabila kelikatan ricih (\(\eta_0\)) telah diplotkan terhadap [2-NaOC_6H_4CO_2Na]. Ini menunjukkan, secara tidak langsung, kemungkinan wujudnya misel cecacing sedangkan kemungkinan wujudnya misel sfera diungkapkan pada [C16E20] \(\geq\) 0.006 M. Sebuah kajian yang sama, dengan ion-lawan yang berbeza, 3,5-Cl_2C_6H_4CO_2^- juga dilaporkan. Nilai purata K_X^Br atau R_X^Br, untuk larutan CTABr/3,5-Cl_2C_6H_4CO_2Na/H_2O (mK_X^Br atau mR_X^Br = 198) adalah hampir 2½ kali lebih besar daripada CTABr/3,5-Cl_2C_6H_4CO_2Na/C16E20/H_2O (mK_X^Br atau mR_X^Br = 78). Keputusan rheometrik untuk larutan 0.015 M CTABr/3,5-Cl_2C_6H_4CO_2Na/H_2O pada 35 °C menunjukkan bahawa plot kelikatan ricih (\(\eta_0\)) terhadap [3,5-Cl_2C_6H_4CO_2Na] mempunyai dua maksima pada dua kepekatan yang berbeza untuk 3,5-Cl_2C_6H_4CO_2Na (0.015 dan 0.04 M) dan ini juga menunjukkan kemungkinan wujudnya misel cecacing. Sebaliknya, kemungkinan pembentukan misel sfera untuk larutan CTABr/3,5-Cl_2C_6H_4CO_2Na/C16E20/H_2O ([CTABr]_t = 0.015 M dan [C16E20]_t = 0.006 M) diperhatikan pada suhu yang sama. Kesalahan CTABr-C16E20 terhadap 4-ClC_6H_4CO_2^- juga telah disiasat. Nilai min K_X^Br atau R_X^Br masing-masing diperolehi untuk larutan CTABr/4-ClC_6H_4CO_2Na/H_2O solution (K_X^Br or R_X^Br = 50) adalah 2.3 kali lebih
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(iii) My daughter (Hafsa Ibrahim Isah)

May their departed souls rest in eternal peace, Ameen.
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<th>Description</th>
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<tr>
<td>°C</td>
<td>Degree celsius</td>
</tr>
<tr>
<td>μM</td>
<td>Micromole</td>
</tr>
<tr>
<td>[ ]_s</td>
<td>Specific concentration</td>
</tr>
<tr>
<td>[ ]_t</td>
<td>Total concentration</td>
</tr>
<tr>
<td>[MX]_{op}</td>
<td>Optimum values of [MX] needed to expel both HO⁻ and Br⁻ from micellar pseudophase to aqueous phase</td>
</tr>
<tr>
<td>[PhS⁻]₀</td>
<td>Initial concentration of ionized phenyl salicylate</td>
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<tr>
<td>Aₐ∞</td>
<td>Observered absorbance at time = ∞</td>
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<tr>
<td>Aₐobs</td>
<td>Observed absorbance</td>
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<tr>
<td>C₁₆E₂₀</td>
<td>Polyethylene glycol hexadecyl ether</td>
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<td>CM</td>
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<td>CMC</td>
<td>Critical micellar concentration</td>
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<td>CₙEₘ</td>
<td>Nonionic micelles</td>
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<td>CₙIM</td>
<td>Ionic surfactants</td>
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<td>Carboxylate ion</td>
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<tr>
<td>CTABr</td>
<td>Hexadecyl/Cetyltrimethylammonium bromide</td>
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<td>DDMAO</td>
<td>Dodecyldimethylamine oxide</td>
</tr>
<tr>
<td>DHC</td>
<td>District heating and cooling</td>
</tr>
<tr>
<td>Dₙ</td>
<td>Detergent/micelles/nanoparticles</td>
</tr>
<tr>
<td>Eq.</td>
<td>Equation</td>
</tr>
<tr>
<td>Fₓₛ</td>
<td>Empirical constant whose magnitude should be (by definition) &gt; 0 and ≤1</td>
</tr>
<tr>
<td>ISI</td>
<td>Institute for scientific information</td>
</tr>
<tr>
<td>k₀</td>
<td>Rate constant at [MX] = 0</td>
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\( k_{n}^{2} \): Nucleophilic second-order rate constant for the reaction of Pip with anionic PS\(^{-}\)

\( k_{W}^{2} \): Nucleophilic second-order rate constant for the reaction of Pip with PS\(^{-}\) in nonionic micellar phase

\( K_{Br} \): Micellar binding constant of Br\(^{-}\)

\( K_{Br/S} \): Empirical constant whose magnitude shows the tendency of Br\(^{-}\) to expel S\(^{-}\) from cationic micellar pseudophase to aqueous phase

\( K_{Br/S}^{n} \): Normalized values of \( K_{Br/S} \)

\( k_{calc} \): Calculated pseudo first order rate constant

\( K_{eqS} \): Equilibrium constant for the micellization of ester molecules (S)

\( k_{M} \): Rate constants for the hydrolysis of the micellized ester (S)

\( k_{obs} \): Observed pseudo first order rate constant

\( k_{obs}^{0} \): Average of higher values of \( k_{obs} \)

\( k_{obs}^{M_{2}X\ (max)} \): \( k_{obs} \) at maximum value \([M_{2}X]\)

\( k_{obs}^{MX\ (max)} \): \( k_{obs} \) at maximum value \([MX]\)

\( K_{S} \): Micellar binding constant of PS\(^{-}\)

\( K_{S}^{0} \): \( K_{S} \) in the absence of X\(^{-}\)

\( k_{W} \): Rate constants for the hydrolysis of the aqueous ester

\( K_{X} \): Micellar binding constant of X\(^{-}\)

\( K_{X/S} \): Empirical constant

\( K_{X/S}^{\alpha} \): Empirical constant whose magnitude shows the tendency of X\(^{-}\) to expel S\(^{-}\) from cationic micellar pseudophase to aqueous phase

\( K_{X/S}^{\alpha} \): Normalized values of \( K_{X/S} \)

\( K_{X}^{Br} \): Conventional ion exchange/counterion binding constants for ion-exchange process X\(^{-}\)/Y\(^{-}\)
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<th>Symbol</th>
<th>Definition</th>
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</tr>
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<td>M</td>
<td>Molarity</td>
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<td>m</td>
<td>Mixed micelles</td>
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<td>Milimole</td>
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<td>MMPP</td>
<td>Multiple Micellar Pseudophase</td>
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<tr>
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<td>Substrate/Ester</td>
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<tr>
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<td>Second</td>
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<tr>
<td>SEK</td>
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<td>SER</td>
<td>Surfactant-enhanced remediation</td>
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<td>Micellized substrate/ester molecules</td>
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CHAPTER 1: GENERAL INTRODUCTION

1.1 Background of the research

1.1.1 Surfactants in water

The word “SURFACTANTS” is a short form of “Surface Active Agents/Ingredients;” (Karsa, 2006). It represents any substance with the properties of absorption and wetting thereby lowering the surface tension of an aqueous solution. They allow easier spreading between two different phases (Holmberg et al., 2002; Tripathy et al., 2017). They can also be expressed as molecules or compounds that play a role in decreasing the tensions at the surface/interface of two different phases (Drew, 2006; Tripathy et al., 2017). This reduction in tensions is directly proportional to the amount of the molecules at the boundary of the phases (Drew, 2006).

In the context of aqueous solutions, surfactants molecules are “amphiphilic” which is a Greek word meaning that the solutes have dual characteristics: amphi which means "dual or double", and then the philos which shows friendship or affinity. These dual characteristics emerge because a solute molecule contains both hydrophobic and hydrophilic parts. They have well differentiated polar and non-polar portions with measurable aqueous solubility as both aggregates and monomers (Salager, 2002).

There are abundant naturally occurring surfactant molecules (polar lipids) which are usually organic substances and exist in living matters (Doehlert et al., 2010; Romantsov & Wood, 2016). The manufacture of affordable synthetic surfactants, used in petrochemical and oilfield industries, has been reported elsewhere (Foley et al., 2012). In addition, Willcox reported that the naturally occurring surfactants (also called alkali soap) were used as domestic cleaning detergent for more than 20 decades ago (Willcox, 2000). These stages of development in the productions of surfactants prompted its scientific and industrial advancement (Drew, 2006; Holmberg et al., 2002).
Surfactants are believed to have influence in quite some fields in chemical and technological processes of fundamental and applied sciences (Drew, 2006). Their molecules consist a polar (or a positively/negatively charged) hydrophilic head group (having a strong affinity to water interface) and a non-polar hydrophobic tail group (usually an alkyl chain which does possess the features of the later) (Cetin & Nasr-El-Din, 2017). This particular duality behavior of surfactants in an aqueous system results on their different types of complex self-aggregation/assembly in the bulk of aqueous solution (Chakraborty et al., 2005; Drew, 2006; Farías et al., 2009; Islam & Kato, 2003a, 2003b). Their molecules also dissolve in the bulk of the aqueous solution to produce monolayers (when spontaneously adsorbed at the air-water interface) as a result of their preferential surface active characteristics (Islam & Kato, 2003a).

1.1.2 Different types of surfactants

Surfactants are of the various types, based upon the nature of their hydrophobic parts. Their tendency to influence certain biochemical processes has been reported to be associated with their composition (the hydrophilic headgroups being the polar parts and the non-polar segments as hydrophobic tail) (Roy et al., 2014). Depending on a specific and intended application, their components differ when either the headgroups or the tails are modified. Aromatic rings (Sigoillot & Nguyen, 1992), Heteroatoms components, for instance; fluoro (Park et al., 2007), siloxane (Sadegh & Naghash, 2015) and naphthalenes (Abdel-Raouf et al., 2011) are also part of the nonpolar tails of some surfactants. This non-polar hydrophobic component may also be primary, secondary of tertiary saturated and/or unsaturated hydrocarbon chain with a different number of carbon atoms (eight to 16) (Clint, 2012; Khan, 2006). Drew as well as Foley and his coworkers have independently reported the presence of the hydrophobic tail of surfactants in the derivatives of both synthetic and natural polymers (Drew, 2006; Foley et al., 2012).
The characteristics of a particular surfactant headgroups are the basis of their classification, and the four major types are classified as cationic, anionic, zwitterionic, and nonionic (Cetin & Nasr-El-Din, 2017; Cullum, 1994). Table 1.1 presents some examples of the various types of surfactants and their components. Quite some studies, nowadays, on different type surfactants have been industrially and academically paid serious attention in the field of nanoscience and nanotechnology due to their specific features (Deda & Araki, 2015; Otzen, 2015).

Table 1.1: Examples of various types of surfactant and their two different components.

<table>
<thead>
<tr>
<th>Surfactant types</th>
<th>Molecules</th>
<th>Headgroups</th>
<th>Tails</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic (e.g. CTABr)</td>
<td>CH₃–(CH₂)₁₅–N⁺(CH₃)₃Br⁻</td>
<td>N⁺(CH₃)₃Br⁻</td>
<td>CH₃–(CH₂)₁₅–</td>
</tr>
<tr>
<td>Anionic (e.g. SDS)</td>
<td>CH₃–(CH₂)₁₁–SO₂–O⁻Na⁺</td>
<td>SO₂–O⁻Na⁺</td>
<td>CH₃–(CH₂)₁₁–</td>
</tr>
<tr>
<td>Zwitterionic (e.g. DDMAO)</td>
<td>CH₃–(CH₂)₁₁–N⁺(CH₃)₂–O⁻</td>
<td>N⁺(CH₃)₂–O⁻</td>
<td>CH₃–(CH₂)₁₁–</td>
</tr>
<tr>
<td>Nonionic (e.g. C₁₆E₂₀)</td>
<td>CH₃–(CH₂)₁₅–(O–(CH₂)₂₀–OH)</td>
<td>(O–(CH₂)₂₀–OH)</td>
<td>CH₃–(CH₂)₁₅–</td>
</tr>
</tbody>
</table>

*Polyoxyethylene glycol (20) hexadecyl ether (Brij 58).

1.2 Aims and objectives

As discussed in section 1.1, the vast importance of different types of surfactants nowadays prompted the study on relatively less number of the literature for mixed surfactants systems in the form of cationic-nonionic. It has been established that addition of nonionic surfactant in an aqueous solution of cationic ones not only reduces the value of relative counterion binding constant but also causes cationic micellar structural growth (Gao et al., 2002). The nonionic surfactant acts as an additive which can be used to achieve the desired cationic micellar structure and viscoelastic behavior (Kamada et al., 2014). The following are the aims and objectives of the research;

(i) To discover probable quantitative correlation between the relative counterion binding constants, $K_{X}^{Br}$ or $R_{X}^{Br}$, and the structural growth of cationic CTABr (hexadecyltrimethylammonium bromide) micelles.
(ii) To study the changes in the values of $K_X^{Br}$ or $R_X^{Br}$ for CTABr/MX/H$_2$O or CTABr/M$_2$X/H$_2$O solution in the presence of different counterions, $X$ ($X = Br^-$, 2-NaOC$_6$H$_4$CO$_2^-$, 3,5-Cl$_2$C$_6$H$_3$CO$_2^-$ and 4-ClC$_6$H$_4$CO$_2^-$).

(iii) To study the changes in the values of $K_X^{Br}$ or $R_X^{Br}$ in CTABr/MX/H$_2$O or CTABr/M$_2$X/H$_2$O solution in the presence of a nonionic surfactant, C$_{16}$E$_{20}$ (where MX and M$_2$X are inert organic salts and $C_{16}E_{20} = C_{16}H_{33}(OCH_2-CH_2)_{20}OH$).

(iv) To use the rheometric measurements of both CTABr/MX/H$_2$O or CTABr/M$_2$X/H$_2$O and CTABr/MX/C$_{16}$E$_{20}$/H$_2$O or CTABr/M$_2$X/C$_{16}$E$_{20}$/H$_2$O (MX = NaBr, 3,5-Cl$_2$C$_6$H$_3$CO$_2$Na and 4-ClC$_6$H$_4$CO$_2$Na and M$_2$X = 2-NaOC$_6$H$_4$CO$_2$Na) solutions in ascertaining the cationic micellar structural changes with the variations in the values of $K_X^{Br}$ or $R_X^{Br}$.

The introduction of the mixed micellar system has been skillfully achieved in changing the CTABr micellar structural transition. This method does not require a change in added salt, pH, temperature, and other factors, for the modification. Thus, the present method is providing more reliable and precise way to alter the cationic micellar structure.

1.3 Likely benefits of the research

Most of the commercially used surface active substances comprise of mixed surfactants systems is because of their relatively lower cost than that of pure surfactants (Khan, 2006). Furthermore, the performance of micelles of pure surfactants systems (due to their good response to concentrations and compositions optimisation for various purposes) is comparatively poor than that of the mixed surfactants system (Christian & Scamehorn, 1995; Holland & Rubingh, 1992). There are several potential benefits of mixed cationic-nonionic micellar systems in modern science and technology. Some of the likely advantages of the research are briefly discussed below;
(i) The district heating and cooling (DHC) systems are vital applications of drag reducers where recirculation of fluid is needed. Polymers that are vulnerable to shear stresses cannot operate effectively but the use of mixed surfactants reduces costs for pumping energy, capital investments, and operation (Ezrahi et al., 2006).

(ii) As wormlike micelles come in contact with petroleum products from the fracture, they are transformed into less viscous spherical micelles, thereby facilitating the flow of residues out of the pack and fracture (Walker, 2001).

(iii) Adding a small quantity of anionic perfluoropolyether surfactants, PFPE-Na to CTABr solution enhances the surface properties and wetting of the mixed micellar system. Therefore, the application of cost could also be reduced. In addition, the mixed micellar systems can form vesicles which could extend the applications as drug delivery vehicles or as micro/nano templates for material synthesis (Hentze et al., 2003; Lipowsky & Sackmann, 1995; Ojogun et al., 2009; Wang et al., 2017; Xiao, 2005).

1.4 Thesis outline and structure

The thesis comprises of six different chapters. Chapter one discusses the background of surfactants, where their amphiphilic nature due to a polar hydrophilic head and a nonpolar hydrophobic tail are discussed. Availability of natural and synthetic surfactants are also discussed. Their different types (cationic, anionic, zwitterionic and nonionic) are highlighted. The aims and objectives, and possible benefits of the research are also included in this chapter. Chapter two presents the survey on the relevant literature where different types of micelles are reviewed. Counterion binding constants, micellar models and viscoelastic nature of micelles are thoroughly discussed. Chapter three and four report, respectively, the findings on counterions, 2-NaOC₆H₄CO₂⁻ and 3,5-Cl₂C₆H₃CO₂⁻ while chapter five reports on 4-ClC₆H₄CO₂⁻. These chapters (chapter three, four and five) are presented in such a way that each chapter provides a report on experimental details,
results, discussion, and conclusion based on a particular organic salt used. The last chapter (chapter six) concludes on the research outcome, from chapter three, four, and five, where the influence of C\textsubscript{10}E\textsubscript{20} on the relative counterion binding constants, K\textsubscript{X}\textsuperscript{Br} or R\textsubscript{X}\textsuperscript{Br}, and counterion-induced CTABr micellar structural growth are highlighted. Recommendations on the directions of future work are also given in the conclusions chapter.
CHAPTER 2: LITERATURE REVIEW

2.1 History of micelles (Nanoparticles) and CMC

Challenges and looking forward to solutions for certain problems have no specific history since the beginning of the world; as one challenge is tackled with, or a problem is solved, a room for more and more to emerge would then be opened. However, in search for a way out of a particular challenge or problem, there should either be a positive or a negative outcome at the end. Both results are useful in the field of research as they can be used to build on the previous work, or to avoid in future. Strive for knowledge opens the sky for researchers to propose whatever type of idea they have as long as it does not violet the fundamentals of its subject. "Nonsense, McBain" were the words uttered by an eminent scientist, chairman of a meeting of the Royal Society in London, responding to the proposal submitted by McBain (McBain, 1944) that surfactants, might aggregate in aqueous solution. Subsequent events confirmed that the nub of McBain’s model was correct (Vincent, 2014). The enormous industry based ‘soaps’ and detergents prompts intensive studies of these complicated systems, supported by monographs and detailed reviews (Menger, 1979).

In early 20th century (1913), McBain introduced (for the first time) the word “micelle” in his attempt to explain the process of molecular self-assembly in an aqueous solution of detergent or soap (Vincent, 2014). When small amounts of a given surfactant are gradually added to a given volume of water, the properties of the aqueous solutions are unexceptional until the surfactant exceeds a specific concentration called the critical micellar concentration, CMC. At this point, further added surfactant exists in solution as aggregates of generally 20 to 100 monomers, which are called micelles. This CMC is acting as a very narrow gateway of surfactants concentration which provides sudden variation in many physicochemical properties, e.g. reaction rates, turbidity, surface tension, magnetic resonance, and others (Drew, 2006). The formation of micelles is often
observed by a change in the pattern of the dependence of a given property of a solution on surfactant concentration (Figure 2.1). This property can be surface tension, the molar conductance of an ionic surfactant, UV-visible absorption spectra of water-soluble dyes (or an iron complex) (Clint, 1992).

**Figure 2.1:** Physical properties of the aqueous solutions of micelles against the total amount of surfactant, [Surf]. The intersection in each pair of linear plots represents the CMC.

When more surfactant is added, the micelles cluster forms more complex aggregates. Micelles are not formed by the gradual association of monomers, forming dimers, trimers, and so on. Rather micelles are examples of organised structures spontaneously formed by simple molecules. A quoted aggregation number is not a stoichiometric number. As the hydrophilic ends of surfactants are attracted to the surface of the polar phase, they line up with it. Micelles of different shapes will begin to form (depending on their concentrations) when the phase is filled up (Evans & Wennerstrom, 1994).

The formation of micelles depends on various factors which include surfactant type, pH, temperature, additives, counterion binding (for ionic surfactants). Surfactant type is one of the major factors affecting the micellization process. The non-polar hydrophobic
tail groups (alkyl chain) of the molecules interact freely among themselves owing to the formation of micelles whereas the charged/polar hydrophilic head groups (for ionic surfactants) exhibit opposing repulsion (Crook et al., 1964). More charged heads have significant influence on micellization process and possess higher CMC value because it will be difficult to overcome the head to head repulsion of the groups as they come to aggregate (Anacker & Ghose, 1968). In general, cationic surfactants have a relatively higher value of CMC, followed by the anionic (Holmberg et al., 2002). Nonionic surfactants have a lower value of CMC due to micellar stabilisation by the alkyl chain (Islam & Kato, 2003b). Also, different tail groups of various surfactants have an influence on micellization process by a change in some carbon atoms in the group. An increase in some carbon atoms in the chain brings about a decrease in the value CMC (Lin et al., 1974). Ali and his co-workers (2014) reported that presence of amino acid additives; glycine, diglycine, and triglycine, favours the CTABr micelle formation by decreasing the value of the CMC (Ali et al., 2014). The CMC exhibits a decreasing pattern as the length of the alkyl chain increases from glycine to triglycine. They concluded that it was the result of increased solvation of CTA⁺ by water molecules and other factors. This solvation increases as the hydrophobicity increase from glycine to triglycine (Ali et al., 2014).

Nature of counterions can also affect the micellization process. Polarizability of a particular counterion will tell whether the CMC value required is less or more. Counterions with higher polarizability results in less CMC value as well as more aggregation number (Ruckenstein & Beunen, 1988). It has been reported by Cheng (2015) that in aqueous solution, the presence of counterions decreases the CMC of mixed surfactant systems because the counterionic salts screen the ionic charge of the polar hydrophilic headgroups. Consequently, reduce the electrostatic repulsion between them in the micelles phase (Cheng et al., 2015). They further concluded that the CMC decreases
with increase in the concentration of the counterion and the relatively stronger electrolyte, Br\(^-\), decreases the CMC most compared to the weaker Cl\(^-\) (Cheng et al., 2015).

2.2 Micelles of mixed cationic-nonionic surfactants system

Pure ionic or non-ionic surfactant molecules in aqueous solution produce what is considered as “micelles” or “normal micelles”. In addition to this category, another type of micelles made up from a combination of monomers of two different/similar micelle-forming surfactants (such as ionic-ionic, nonionic-nonionic or ionic-nonionic surfactants with various features) in aqueous solutions are regarded as “mixed micelles” (Rathman & Scamehorn, 1984). Due to the availability of various surfactants, different types of the mixture are likely to provide different features and application fields (M. N. Khan, 2006). The mixed surfactants micellar system for the present research is strategically chosen to be cationic-nonionic because their intensive investigations in the last almost three decades were only on the physicochemical properties (Alargova et al., 2001; Esumi et al., 1998; Ghosh & Moulik, 1998; Griffiths et al., 1999; Islam et al., 2002; Palous et al., 1998; Shiloach & Blankschtein, 1998; Yoshida & Dubin, 1999). The current research is different as it discusses quantitatively the effects of mixed micelles on the reaction rates together with some empirical approaches (Khan, 2015). This method requires the investigation of the structural behaviours of the mixed micelles. It is believed that the energy processes during formation of mixed micelles are almost the same as those during the formation of pure micelles. Therefore, the mixed micellar structural transitions are relatively similar to those of pure micelles. It has been understood that a solution of mixed micelles of two different surfactant y and z, y behaves as an additive for z and the vice versa (Khan, 2015).
2.3 Micellar growth

Due to their amphiphilic behavior, surfactant molecules can aggregate in solution to form different microstructures. At concentration similar to CMC, the micellar structure is spherical or rodlike (Menger, 1979; Schramm et al., 2003; Wennerström & Lindman, 1979). However, several factors (such as temperature, pH, increase in concentration of micelle-forming surfactant, additives) affect the shape and size, causing the micellar structural transition/growth (Cates & Candau, 1990; Davies et al., 2006; Kern et al., 1991; Kumar et al., 1996; Patel et al., 2014; Yin, et al., 2006). The morphology of spherical micelles can be skillfully altered to provide different micellar structures such as wormlike, rodlike, or vesicles by the use of specific additives (Figure 2.2). Hence, by the proper choice of a specific factor, the micelles can be manipulated to obtain different micellar structures. These self-assemblies provided significant importance for applications in various industries as well as modern technology, for instance, drag reduction, enhanced oil recovery, drug delivery (Karayil et al., 2016).

The addition of certain inorganic or organic salt, as counterions, to micellar aggregates of a spherical structure, also induces the formation of wormlike micelles (Hayashi & Ikeda, 1980; Ikeda et al., 1980). Bijma and co-authors reported (Bijma et al., 1998) that the nature of counterion among other factors influencing the growth of spherical micelles to wormlike micelles. Depending upon the type and molecular nature of the surfactant cationic headgroup and the position of the substituent in the aromatic counterion, wormlike micelles may be formed. They concluded that the growth is largely dependent upon the nature and structure of the counterion.
Figure 2.2: Micellar growth as a result of additives.

The CTABr micellar growth has been investigated by different methods such as small angle X-ray scattering (Hirata et al., 1988), dynamic light scattering (Dorshow et al., 1982; Kuperkar et al., 2011; Nemoto & Kuwahara, 1993), viscosity measurement (Inoue et al., 2005; Kim & Yang, 2000), small angle neutron scattering (Aswal et al., 1998; Mata, Aswal et al., 2006), and static light scattering (Brown et al., 1989). Patel and coauthors (2014) have also examined the pH-induced CTABr micellar growth in the presence of p-toluic acid, p-toluidine, and p-cresol as weakly polar aromatic additives by different techniques (Patel et al., 2014) and concluded that interaction between the aromatic additives and CTABr micelles brought about the micellar structural growth from spherical to extended ellipsoidal micelles (Patel et al., 2014).

It is, therefore, a common perception that different factors including temperature, pH, increase in the concentration of micelle-forming surfactant, additives, could appropriately be used to change the morphology (shape and size) of surfactant micelles, which is the leading cause for the micellar structural transition/growth.
2.4 Applications

Because of their encounter in almost all domestic and industrial importance, micelles of mixed surfactants system have been the great area of research interest in the field of colloids and interfaces (Hoffmann & Pössnecker, 1994; Holland & Rubingh, 1992; Rosen, 1986; Shiloach & Blankschtein, 1998). There are quite some potential applications of the mixed cationic-nonionic micellar medium. They cover a broad range of industrial processes (from oil and gas, pharmaceutical, cosmetics, to mention but few). Some of the applications of mixed micelles include but not limited to the following:

a) Some studies reported that curcumin (with enol-keto tautomeric ability) could be soluble in the aqueous micellar solution of triblock copolymer of polyethylene oxide and polypropylene oxide, Pluronic P123 (PEG-PPG-PEG), by simply heating the solution. In drugs delivery to a specified target, less solubility of curcumin and its poor bioavailability becomes a great challenge (Anand et al., & Aggarwal, 2007; Ganguly et al., 2017; Hatcher et al., 2008). However, the micellar system of ionic and nonionic surfactants mixture could be a method to the solubilization (Ganguly et al., 2017). These micelles are very useful to enhance the movement of the drug into the blood brain and intestine barriers. They are also found to be good in mediating the drug effectiveness over multidrug-resistant cancer cells (Batrakova & Kabanov, 2008; Batrakova et al., 2010).

b) Due to their increase in bioavailability and tendency to make the polyaromatic hydrocarbons soluble in aqueous solution, cationic-nonionic surfactant mixtures are extremely, nowadays, used in environmental remediation (for surfactant-enhanced remediation, SER) (Liang et al., 2017; Mao et al., 2015; Shah et al., 2016). When the ionic surfactant concentration reaches CMC, the micelles behave as hydrocarbon-like phase and enhance the partition of polyaromatic hydrocarbons into aqueous solutions (Liang et al., 2017). The relatively weaker
repulsion in nonionic surfactants influences the headgroups to form aggregate and larger micelles. These micelles have higher affinity to polyaromatic hydrocarbons in ionic surfactants (Dar et al., 2007; Liang et al., 2017).

2.5 Amminolysis/piperidinolysis of ester

The general reaction for the piperidinolysis of ester can represented as secondary aminolysis as shown in Scheme 2.1.

Scheme 2.1: General acid/base piperidinolysis of ester

The acid catalysed reaction of piperidine with ester increases the rate of both forward (\( k_f \)) and backward (\( k_b \)) reaction (i.e., it favours the formation of N-alkyl salicylate and ester). In the other hand, if the rate of reaction is base catalysed, Scheme 2.1 will no longer be reversible as the product, N-alkyl salicylate, is comparatively a stronger than the conjugate acid, 2° amine (in this case piperidine). Hence, \( R_1O^- \) undergoes irreversible reaction with N-alkyl salicylate to yield more stable ionized N-alkyl salicylate as product. Therefore, a base cannot catalyse the rate of reversible reaction between phenol and N-alkyl salicylate.

2.6 Proposed micellar mechanisms

The set-up of larger number of the reaction mechanism were best determined using kinetic studies. These were achieved by the use of data obtained (with respect to the reaction rates) under certain conditions. The proposed reaction mechanisms were considered for the use of the derived kinetic equations (Khan, 2006). Scheme 2.2 illustrates a brief reaction mechanism in which a bimolecular system is involved with \( k_M \).
representing second-order rate constant for two reactions at both micellar and aqueous interfaces. Subscript M and W denote micellar and aqueous phases, respectively. The reactant, $R$, $K_R$ and $K_S$ are the respective equilibrium constants for the reactants and substrate (ester).

For the majority bimolecular reactions which are mediated by micelles, the parallel steps for the reactions are reported to occur at the same time in the two different phases as demonstrated in scheme 2.2. However, comparatively small number of reports have presented different results. The drawback is related different factors, such as possible occurrence of cross-interface reaction (Bunton & Romsted, 1979; Vera & Rodenas, 1986; Bunton & Moffatt, 1986; Ortega & Rodenas, 1987).

\[
\begin{align*}
S_W & + D_n & \xrightleftharpoons{K_S} & S_M \\
R_W & + D_n & \xrightleftharpoons{K_R} & R_M \\
S_W & + R_W & \xrightarrow{k_W^2} & \text{Product(s)} \\
S_M & + R_M & \xrightarrow{K_W^M} & \text{Product(s)}
\end{align*}
\]

Scheme 2.2: Micellar-mediated bimolecular reaction mechanism.

2.7 Micellar models and their conditions/assumptions

Until mid-1960’s, the qualitative explanations of the observed kinetic results on the rate of micellar-mediated reactions were the only available and reliable ways of data interpretation. This was due to the absence of acceptable kinetic model which could describe, logically and convincingly, the mechanisms of micellar-mediated reactions. Some years later (late 1960’s), the quantitative explanations were possible due to the availability of kinetic micellar models which could be enough for the interpretations of kinetic data on micellar-mediated reactions. Despite the fact that all the models appeared to be imperfect (Khan, 2006), their emergence provided a merely perfect or comparatively
perfect model (Khan, 2006). Some of the micellar kinetic models, developed so far, were examine to understand the quantitatively the effects of micelles on the reaction rates. These models and their assumptions are discussed in the subsequent subsections.

2.7.1 Pre-equilibrium micellar kinetic model

This is also called Menger’s phase separation model or enzyme-kinetic-type model. The different experimentally obtained values of micellar-mediated reaction rate constants were used to demonstrate their response over the change surfactant concentration. The increase in surfactant concentration shows either a monotonic decrease or increase in the values of the rate constant (Figure 2.3). As reported by Menger and Portnoy (1967) (Menger & Portnoy, 1967), the anionic and cationic micellar-mediated hydrolysis of some esters follow the pattern in Figure 2.3.

![Graph of k_\text{obs} vs. [D_n] showing a monotonic increase (a) and decrease (b) in k_\text{obs} with the increase in [D_n].](image)

**Figure 2.3:** Graphs of $k_{\text{obs}}$ vs. $[D_n]$ showing a monotonic increase (a) and decrease (b) in $k_{\text{obs}}$ with the increase in $[D_n]$.

They suggested the reaction pathway illustrated in Scheme 2.1 where $K_\text{eqS}$ and $P$ represent, respectively, the equilibrium constant for the micellization of ester molecules (S) and the product of the reaction. $D_n$, $S_w$, and $S_M$ represent aqueous/free ester and
micellized ester molecules, respectively. Symbols $k_W$ and $k_M$ denote the respective rate constants for the hydrolysis of the aqueous and micellized ester.

\[ \text{Scheme 2.1: Reaction pathways for the unimolecular reaction based on pre-equilibrium kinetic, PEK, micellar model.} \]

The PEK micellar model has the following assumptions:

i. The unassociated surfactant concentration remains constant above the CMC. Therefore, the expression $[D_n] = \{[\text{Surf}]_T - \text{CMC}\}/n$ should hold with $[\text{Surf}]_T$ standing for total surfactant concentration and $n$ representing the average number of surfactant micellar aggregate.

ii. The formation of micelles occurs at exactly the CMC (not within the certain small range of concentration).

iii. The formation of micelles is not disturbed/interrupted by the substrate.

iv. The stoichiometric ratio between the substrate and the micelles should be in the form of 1:1.

v. There will be no formation of complex molecules between the surfactant monomer and the substrate.

The relationship between the pseudo first order rate constant, $k_{obs}$, and the illustration in Scheme 2.1 gives Eq. 2.1 for several micellar models (Bunton & Savelli, 1986; Menger & Portnoy, 1967).

\[ k_{obs} = \frac{k_W + k_M K_S[D_n]}{1 + K_S[D_n]} \quad (2.1) \]
2.7.2 Pseudophase micellar model

At \([\text{Surf}]_T\) below and beyond the CMC, an aqueous solution of the surfactant is transparent to UV-visible radiation. This is regarded as a micellar single homogeneous phase and, in this case, the micelles are not being able to form a real phase (Khan, 2006). With this reason, some reports (Bunton \textit{et al.}, 1991; Rathman, 1996) proposed the idea of pseudophase model to be considered, instead of a real micellar model. The pseudophase, PP, micellar model retains all the assumption in PEK (Menger & Portnoy, 1967) with the addition of other assumptions as explained thoroughly elsewhere (Khan, 2006). The details of this model could be found in several reports (Bunton, 1991, 1997; Bunton \textit{et al.}, 1993).

2.7.3 Pseudophase ion exchange micellar model

The concept of pseudophase ion exchange, PIE, model was developed based upon the competition (exchange) between counterions (X) and (Y), of similar charge, in an ionic micellar surface. It was independently reported by Romsted and other researchers (Quina \& Chaimovich, 1979; Romsted, 1977) and it provides the quantitative or semi-quantitative explanations of ion exchange. The PIE micellar model is an extension of PP model and, hence, it retains all the assumptions involved in PEK and PP models with the addition of some more assumptions as highlighted in various excellent literature reports (Bunton, 1979, 1991, 1997; Bunton \textit{et al.}, 1991; Bunton \& Savelli, 1986; Romsted, 1977). The assumptions and the theories and concepts are discussed in detail elsewhere (Khan, 2006).

The PIE model of micelles was initially provided to explain, quantitatively, the data obtained from several bimolecular kinetic reactions related to a monovalent ion exchange process involving reverse micelles (Quina \& Chaimovich, 1979), aqueous ionic micelles (Bunton \textit{et al.}, 1991), and cosurfactant modified micelles (El Seoud \& Chinelatto, 1983;
Pal et al., 2005). Based on this model, a study on the effect of [MX] (where MX = KBr) on the rate of hydrolysis of some esters (S) in the presence of ionic CTABr micelles was reported (Vera & Rodenas, 1986). The observed data (k_{obs} vs. [MX]) were discussed according to the PIE model coupled with an empirical equation (Eq. 2.2)

\[ K_S = K_S^0 - L [MX] \]  \hspace{1cm} (2.2)

where \( K_S \) is the cationic CTABr micellar binding constant of \( S^- \), \( K_S^0 = K_S \) at \([MX] = 0\) and \( L \) is an empirical constant whose magnitude is the measure of the ability of \( X^- \) to expel \( S^- \) from the cationic CTABr micellar pseudophase to the aqueous phase (Khan, 2006).

The limitation of PIE model has been noticed in some cases, where the concentration of surfactant is very high or the salt (additive) contains (in excess) a strong hydrophilic counterion such as F\(^-\), Cl\(^-\) and HO\(^-\) (Bunton, 1991; Bunton et al., 1991; Bunton et al., 1993; Khan & Ismail, 2001). This limitation arose due to the failure of one (or more) of those assumptions provided in the literature (Khan, 2006). Given this, several researchers (Abuin et al., 1983; Blasko et al., 1993) have discussed the probable cause(s) of the limitation and the possible adjustment (Khan, 2006).

### 2.8 Viscoelastic properties of micelles

Due to their various applications (Schubert et al., 2003; Yang, 2002), aqueous viscoelastic surfactant micellar solutions have been reported to be used in pharmaceutical and health sectors (Ideta et al., 2004; Kabanov et al., 2002; Kataoka et al., 2001; Nishiyama et al., 2005; Nishiyama & Kataoka, 2006; Rangel-Yagui et al., 2005; Sutton et al., 2007) as well as petrochemical industries (Qi & Zakin, 2002). The distinctive characteristic of viscoelastic micelles, over polymers in solution, is their tendency to change and regain shapes and sizes when subjected to the external factors such as heat.
and shear. Thus they are regarded as “living polymers” (Yang, 2002; Ziserman et al., 2009). They also attain a certain level of stability under high temperature or high shear rate conditions (Davies et al., 2006).

Though several studies (Ali & Makhloufi, 1997; Shikata et al., 1987; Soltero et al., 1996) have reported that addition of counterionic salts makes the formation of viscoelastic wormlike micelles easier, another study (Gamez-Corrales et al., 1999), later, revealed their formation, in the absence of salts, in cationic surfactant solutions.
CHAPTER 3: INFLUENCE OF MIXED CTABr–C\textsubscript{16}E\textsubscript{20} MICELLES/NANOPARTICLES ON RELATIVE COUNTERION BINDING CONSTANS IN AQUEOUS SOLUTIONS OF INERT SALTS (2-NaOC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}Na AND NaBr): KINETIC AND RHEOMETRIC STUDY\textsuperscript{1}

3.1 Introduction

Micellar substances are nanoparticles in nature, and their molecular, physical and chemical behaviours on the kinetic rate of reaction have been thoroughly investigated for almost sixty years ago (Fendler, 2012). Despite the fact that experimental and theoretical studies on the structure of mixed micelles have been published for the past 20 to 30 years, details of the reactions are not being discussed well when compared to pure ones. Studies on the influence of mixed micelles upon the rate of kinetic reactions began less than 25 years back (Eads & Robosky, 1999; Junquera & Aicart, 2002). Efforts were made to come up with highlights on the majority of data by the use of one of the two models, viz; (i) micellar models of pure surfactant solutions (Muñoz et al., 2002; Zakharova et al., 2003) or (ii) combination of (i) above and empirical equations (Frescura et al., 1995; Lee & Nome, 2000).

Addition of nonionic micelles (C\textsubscript{n}E\textsubscript{m}) to cationic micellar-mediated reaction mixture lowers a number of counterions at the surfaces of ionic surfactants, and hence reduces the fraction of ionic surfactant coverage (β) (Bunton & Savelli, 1987; Larsen & Tepley, 1974). Moreover, the volume of the micellar pseudophase also increases (Vangeyte et al., 2004), which in turn affects the amount of micellized reactant via dilution. The

\textsuperscript{1}This chapter has been published, as journal article, by RSC Advances; Fagge, I. I., Khalid, K., Noh, M. A. M., Yusof, N. S., Zain, S. M., & Khan, M. N. (2016). Influence of mixed CTABr-C\textsubscript{16}E\textsubscript{20} nanoparticles on relative counterion binding constants in aqueous solutions of inert salts (2-NaOC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}Na and NaBr): Kinetic and rheometric study. RSC Advances, 95504-95511. ISI indexed.
pseudophase (PP) micellar model coupled with Eq. 3.1 have been used to analyse the data (Khan & Ismail, 2003).

\[ K_S = \frac{K_S^0}{(1 + K_{X/S}[MX])} \]  

where \( K_S \) is the CTABr micellar binding constant of the anionic reactant, \( S^- \), (and equals to \( K_S^0 \) in the absence of \( X^- \)), \( K_{X/S} \) denotes empirical constant and its values indicate the ability of \( X^- \) to transfer anionic reactant, \( S^- \), from pure CTABr micellar phase to bulk aqueous phase (Khalid et al., 2016). Therefore, \( K_{X/S} \) should be directly and inversely proportional to \( K_S \) and \( K_S^0 \), respectively (Khan & Fui, 2009).

Several efforts have been made to bring reliable clarification(s) for the viscoelastic nature of the micellar systems in the aqueous phase. However, almost all the clarifications are not enough for some systems such as those of CTABr with certain inert salts (Rao et al., 1987). Moreover, there is a scarcity of quantitative and theoretical evidence(s) to confirm that addition of these salts in a surfactant solution results in the viscoelastic behavior of micelles.

The report in this chapter varies from previously reported ones (Khan & Fui, 2009; Khan & Ismail, 2004), due to the fact that it is designed to (i) deal with mixed cationic-nonionic surfactants (CTABr-C\(_{16}\)E\(_{20}\)) and a bimolecular reaction aimed at providing a quantitative elucidation on how the rate of CTABr-C\(_{16}\)E\(_{20}\) micellar catalyzed organic reactions could be affected by the addition of sodium salicylate, (ii) to use rheological information to correlate the values of relative counterion binding constants (\( K_X^{Br} \) or \( R_X^{Br} \)) for CTABr/M\(_2\)X/H\(_2\)O solution (M\(_2\)X = 2-NaOC\(_6\)H\(_4\)CO\(_2\)Na) systems and CTABr micellar structural growth of CTABr/C\(_{16}\)E\(_{20}\)/M\(_2\)X/H\(_2\)O solution under different experimental conditions. The results obtained and their possible elaborations are presented in this chapter.
3.2 Methodology

Two types of experiments were involved in the study; the kinetic measurements for the reaction of piperidine with ionised phenyl salicylate, in the presence of salts and surfactants, which was monitored using a UV-Visible spectrophotometer. The other type was the rheometric study to support the findings from the former.

3.2.1 Materials

Reagent-grade substances, which are commercially available from different manufacturers, have been used. Phenyl salicylate (PSH) was bought from Fluka (% purity ≥ 98). Acetonitrile from Merk (an A.R. Grade) was used in preparing 0.01 M stock solution of PSH. The other reactant, piperidine (Pip), was also supplied by Merk (% purity ≥ 99). The cationic surfactant hexadecyltrimethylammonium bromide (in powdered form), denoted as CTABr, was provided by Sigma-Aldrich (% purity ≥ 99). The nonionic surfactant polyethylene glycol (20) hexadecyl ether \([C_{16}H_{33}(OCH_2CH_2)_{20}OH (C_{16}E_{20})]\), also called “Brij 58”, was purchased from Sigma-Aldrich. Sodium hydroxide, NaOH, with ≥ 99% purity was from Merk. The organic salt disodium salicylate, 2-NaOC_6H_4CO_2Na (M_2X), with % purity ≥ 98, was brought by Sigma-Aldrich whereas the inorganic one, sodium bromide, NaBr (MX), was purchased from Merk with ≥ 99% purity. All these reagents were used without further purification. The stock solutions of 1.0 M Pip, 0.2 M CTABr, 0.2 M C_{16}E_{20}, 0.3 M NaOH, and 2.5 M NaBr were prepared by using distilled deionized water while the standard solution of 0.5 M M_2X (disodium salicylate, 2-NaOC_6H_4CO_2Na) was prepared by adding 0.55 M NaOH to 0.5 M solution of sodium salicylate.

3.2.2 Kinetic method

The thermoregulatory water bath and electronically temperature controlled cells compartments UV-Visible spectrophotometer (equipment model; Perkin Elmer Double
Beam Lambda 25) was used to carry out the kinetic experiments. The measurements were performed to observe the disappearance of ionised phenyl salicylate, PS\(^{-}\), in a solution containing 0.10 M Pip, > 0.03 M NaOH, and NaBr as well as 2-NaO\(_4\)H\(_4\)CO\(_2\)Na, at 370 nm and 35 °C (in the presence of pure CTABr and mixed CTABr-C\(_{16}\)E\(_{20}\) micelles. Distilled deionized water was used as a blank before the measurements. Volumetric flasks, of 25 mL each, containing 4.9 mL mixture of different concentration of the reagents (except PSH) were immersed into a water-bath at 35 °C for at least 15 minutes. Followed by the addition of 0.1 mL of 0.2 mM substrate (PSH) to the flask (total volume became five mL) to initiate the reaction. This went simultaneously with starting the kinetic measurement in the Lambda 25 computer software. The solution was then transferred to the cuvette followed by putting it in the cell compartment. The rate was monitored at different concentrations of MX and M\(_2\)X.

### 3.2.2.1 Product characterization of piperidinolysis of PS\(^{-}\)

The rate and product characterization study on the alkaline piperidinolysis of PS\(^{-}\) in an aqueous solvent containing 2% v/v CH\(_3\)CN, as described in the earlier study (Khan & Fui, 2009), revealed the brief reaction step as represented by **Scheme 3.1**.

![Scheme 3.1: Chemical equation for the aqueous piperidinolysis of PS\(^{-}\).](image)

In **Scheme 3.1**, \(k_n^2\) represents nucleophilic second-order rate constant for the reaction of Pip with anionic PSH (PS\(^{-}\)). The piperidinolysis of PS\(^{-}\) has been shown to involve nonionic PS\(^{-}\) (PSH) and Pip as the reactants and under the experimental condition the
reaction of PSH and Pip is concluded to be kinetically insignificant (Khan, 1991; Khan & Fui, 2009).

The experiment was fixed to fit pseudo first order rate law throughout, by making sure that the ratio of total concentrations of Pip and PS\(^{-}\) ([Pip]\(_T\) : [PS\(^{-}\)]\(_T\)) is 500 : 1 where [ ]\(_T\) stands for the total concentration. The steps for the order of the reaction are illustrated as follows;

\[ S \xrightarrow{k_{obs}} P \] (3.2)

where S and P represent the reactant and the product, and the \(k_{obs}\) is the pseudo first order reaction rate constant for the reaction. The rate law, Eq. 3.2, can be presented as follows;

\[
\text{Rate} = \frac{-d[S]}{dt} = \frac{-d[Pip]}{dt} = \frac{+d[P]}{dt} = k_{obs}[S]
\] (3.3)

or

\[
\text{Rate} = \frac{-d[S]}{dt} = k_{obs}[S]
\] (3.4)

Integrating Eq. 3.3 or 3.4 results in Eq. 3.5

\[ [S] = [S_0] \exp(-k_{obs}t) \] (3.5)

with [S\(_0\)] and [S] representing, respectively, the concentration of S at initial stage (time = 0) and at time, t. Considering \(A_{obs}\) to be the observed absorbance, then

\[ A_{obs} = \delta_S[S] + \delta_P[P] \] (3.6)

where \(\delta_S\) and \(\delta_P\) stand for the molar absorptivities of S and P, respectively.

Recalling Eq. 3.2,
\[ [S_0] = [S] - [P] \] \hspace{1cm} (3.7)

and

\[ [P] = [S_0] + [S] \] \hspace{1cm} (3.8)

Relating Eqs. 3.6 and 3.8,

\[ A_{obs} = \delta_S [S] + \delta_P ([S_0] - [S]) = (\delta_S - \delta_P) [S] + \delta_P [S_0] \] \hspace{1cm} (3.9)

If \( \delta_P ([S_0] = A_{\infty} \) and \( \delta_S - \delta_P = \delta_{app} \) Eq. 3.9 can be modified to Eq. 3.10

\[ A_{obs} = \delta_{app} [S] + A_{\infty} \] \hspace{1cm} (3.10)

Substituting Eq. 3.5 into Eq. 3.10 gives

\[ A_{obs} = [S_0] \delta_{app} \exp(-k_{obs}t) + A_{\infty} \] \hspace{1cm} (3.11)

Eq. 3.11 shows the relationship between the absorbance \( (A_{obs}) \) and the reaction time \( (t) \) for the reaction, and it was used to calculate the values of \( \delta_{app} \) (apparent molar absorptivity), \( k_{obs} \) and \( A_{\infty} \) \( (A_{obs} = A_{\infty} \) at \( t = \infty) \) and the results were analyzed as described elsewhere (Khan & Ismail, 2003). The values of \( k_{obs} \) were obtained in the presence of pure [CTABr]_T and mixed [CTABr]_T-[C_{16}E_{20}]_T micelles at different [MX]. Different values of \( k_{obs} \), in the absence of CTABr, were also determined and are required in the use of the SEK method. Details of this technique and explanations of the reaction mechanisms were according to what was described in the earlier report (Khan & Ismail, 2003).

3.2.3 Determination of relative counterion binding constants \( (K^B_X \) or \( R^B_X) \) for \( X = \text{-OC}_6\text{H}_4\text{CO}_2\text{Na} \) using the semi empirical kinetics technique

Semi empirical kinetic (SEK) method which requires the use of appropriate reaction kinetic probe, has been used experimentally to determine the values of \( K^B_X \) or \( R^B_X) \) for pure
CTABr (Khan & Sinasamy, 2011; Yusof & Khan, 2012). The effect of the concentrations of the inert counterionic salts ([MX] and [M₂X]) on the values of \( k_{\text{obs}} \) for the nucleophilic reaction of Pip with PS\(^-\) at constant concentration of pure CTABr and 35 °C, has been used as a kinetic probe to use the SEK method (Yusof et al., 2013). The determination of \( K_{X}^{\text{Br}} \) or \( R_{X}^{\text{Br}} \) by the use of the SEK method requires the values of kinetic parameters, \( K_{X/S}^{n} \), for \( X = X^- \) (test counterions) and \( \text{Br}^- \) (reference counterion), at a constant [CTABr]\(_T\). The values of \( K_{X/S}^{n} \) were determined by the use of \( K_{S}^{0} (= \text{CTABr micellar binding constant of PS}^- \text{ at [MX] or [M}_{2}\text{X} = 0) \). The reported value of \( K_{S}^{0} \) (7000 M\(^{-1}\)) (Khan & Arifin, 1996) was used to calculate the values of \( K_{X/S}^{n} \). Details of this technique and explanations of the reaction mechanisms are as according to what was described in earlier reports (Khan, 2010; Khan & Ismail, 2003; Khan & Sinasamy, 2011).

3.2.4 Rheological measurements

In these measurements, the total volume of the sample used (for kinetic measurements explained in section 3.2.2), was doubled (i.e. 10 mL). Two different sets of desired samples were prepared, viz; (i) Pure CTABr micellar solution containing a constant volume of > 0.03 M NaOH, 0.10 M Pip, 2 x 10\(^{-4}\) M PSH and 0.015 M CTABr at various [M₂X] ([M₂X] within the range of 0.006 to 0.120 M). (ii) Mixed CTABr-C\(_{16}\)E\(_{20}\) micellar solution containing constant volume of > 0.03 M NaOH, 0.10 M Pip, 2 x 10\(^{-4}\) PSH and [CTABr]\(_T\)-[C\(_{16}\)E\(_{20}\)]\(_T\) (with [CTABr]\(_T\) = 0.015 M and [C\(_{16}\)E\(_{20}\)]\(_T\) = 0.006 M) at various [M₂X] ([M₂X] within the range of 0.006 to 0.120 M). The rheological measurements were conducted at 25 and 35 °C using Anton Paar MCR301 rheometer, with a double gap cylinder (DG26.7/T200/SS having 26.661 mm external diameter and 24.656 mm internal diameter). The values of steady-shear viscosity (\( \eta \)), during the flow curve measurement, were obtained within the range of 0.010-1000 s\(^{-1}\) of shear rates. The details of the experiment were the same described in the previous study (Yusof et al., 2013).
3.3 Results

3.3.1 Effect of [NaBr] on $k_{obs}$ for the piperidinolysis of PS$^-$ at constant concentration of pure C$_{16}$E$_{20}$ and 35 °C

Certain kinetic runs were carried out to study the influence of pure C$_{16}$E$_{20}$ on $k_{obs}$ on the reaction of 0.10 M Pip with 2 x $10^{-4}$ M PS$^-$ and 0.030 M NaOH at various concentrations of NaBr ([NaBr] within the range of 0.000-0.700 M). The experiment was achieved by adding 0.001 M C$_{16}$E$_{20}$ at 35 °C and 370 nm. Similar observations were obtained by increasing [C$_{16}$E$_{20}$]$_T$ to 0.003, 0.006, 0.008, 0.010 and 0.015 M. The values of $k_{obs}$, $\delta_{app}$ and $A_{\infty}$ at [C$_{16}$E$_{20}$]$_T = 0.001$, 0.003 and 0.006, and 0.008, 0.010 and 0.015 M are presented, respectively, as Appendices A and B.

3.3.2 Effect of mixed CTABr-C$_{16}$E$_{20}$ on $k_{obs}$ for the piperidinolysis of PS$^-$ at various [NaBr] and 35 °C

Several kinetic runs were conducted to study the effects of mixed CTABr-C$_{16}$E$_{20}$ on $k_{obs}$ for the reaction of 0.10 M Pip, with 2 x $10^{-4}$ M PS$^-$ and 0.030 M NaOH in the presence of NaBr (within the concentration range of 0.000–0.700 M). These data were used to obtain parameters required to find the value of $K_X^B$ or $R_X^B$. The experiments were carried out by adding three different [CTABr]$_T$ (= 0.006, 0.010 and 0.015 M) at 0.006 M C$_{16}$E$_{20}$, 35 °C and 370 nm. Similar observations were obtained by increasing [C$_{16}$E$_{20}$] to 0.010 M and 0.015 M. The values of $k_{obs}$, are presented in Tables 3.1, 3.2 and 3.3.

3.3.3 Effect of [2-NaOC$_6$H$_4$CO$_2$Na] on $k_{obs}$ for the piperidinolysis of PS$^-$ at constant concentration of pure CTABr and 35 °C

Several kinetic experiments were conducted at 0.006 M CTABr, 0.10 M Pip, 2 x $10^{-4}$ M PSH, $> 0.03$ M NaOH and various [2-NaOC$_6$H$_4$CO$_2$Na] (0.00–0.14 M). Complementary results were found by increasing the concentration of CTABr to 0.010
M and 0.015 M. The values of $k_{obs}$ obtained within [2-NaOC₆H₄CO₂Na] range are presented graphically in Figure 3.1.

3.3.4 Effect of [2-NaOC₆H₄CO₂Na] on $k_{obs}$ for piperidinolysis of PS⁻ at constant concentration of pure C₁₆E₂₀ and 35 °C

Other kinetic experiments for the reaction of 0.10 M Pip with 0.20 mM PS⁻ and 0.030 M NaOH at various [2-NaOC₆H₄CO₂Na] (ranging from 0.00 to 0.12 M) in the presence of C₁₆E₂₀ were conducted. Similar observations were obtained by increasing [C₁₆E₂₀] to 0.003, 0.005, 0.006, 0.007, 0.008, 0.010, 0.012 and 0.015 M.

The observed data, $k_{obs}$ versus [2-NaOC₆H₄CO₂Na] as well as $\delta_{app}$ and $A_{\infty}$, at [C₁₆E₂₀] = 0.001, 0.003, 0.006, 0.008, 0.010 and 0.015 M are presented, respectively, as Appendices C and D.

3.3.5 Effect of mixed CTABr-C₁₆E₂₀ on $k_{obs}$ for piperidinolysis of PS⁻ at various [2-NaOC₆H₄CO₂Na] and 35 °C

To study the influence of mixed CTABr-C₁₆E₂₀ micelles ([CTABr] = 0.006, 0.010 and 0.015 M + 0.006 M C₁₆E₂₀) on the reaction between Pip, PS⁻ and NaOH, different kinetic experiments were conducted in the presence of [2-NaOC₆H₄CO₂Na] (0.00-0.15 M). Similar results were obtained by increasing [C₁₆E₂₀] to 0.010 M and 0.015 M. The values of $k_{obs}$ are outlined and presented, respectively, in Figures 3.2, 3.3 and 3.4.

3.3.6 Rheological behavior of aqueous pure CTABr and mixed CTABr-C₁₆E₂₀ micelles in the presence of various [2-NaOC₆H₄CO₂Na] at 25 and 35 °C

Rheological measurements of solutions (in aqueous form) containing 0.015 M CTABr, constant 0.1 M Pip, 2 x 10⁻⁴ M PS⁻ and > 0.03 M NaOH and different values of [2-NaOC₆H₄CO₂Na] were conducted at the steady-shear rheological response, and 25 and 35°C. The values of shear viscosity ($\eta$) at various shear rates ($\gamma$) were determined at this
condition. These results are presented, using log-log plots of $\eta$ vs $\dot{\gamma}$ at various [2-NaOC$_6$H$_4$CO$_2$Na], in Figures 3.5 (a) and (b) at, respectively, 25 and 35 °C. Measurements on aqueous solutions containing mixed 0.015 M CTABr and 0.006 M C$_{16}$E$_{20}$, with other conditions similar to one mentioned above were also conducted. The values of $\eta$ at various $\dot{\gamma}$ were also determined. Different observations were obtained at the two different temperatures (25 and 35 °C) and the results are presented in Figures 3.6 (a) and (b).
Table 3.1: Pseudo-first-order rate constants ($m_{k_{obs}}$) for the reaction of piperidine with anionic phenyl salicylate (PS$^-$) at 0.006 M CTABr in the presence of 0.006, 0.010, and 0.015 M C$_{16}$E$_{20}$ and different [MX] (= NaBr).$^a$

<table>
<thead>
<tr>
<th>[MX]$^b$ (M)</th>
<th>[CTABr]$_T$$^c$ = 0.006 M</th>
<th>0.006 M</th>
<th>0.010 M</th>
<th>0.015 M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^4 m_{k_{obs}}$ s$^{-1}$</td>
<td>$10^4 m_{k_{calcd}}$ s$^{-1}$</td>
<td>$10^4 m_{k_{obs}}$ s$^{-1}$</td>
<td>$10^4 m_{k_{calcd}}$ s$^{-1}$</td>
</tr>
<tr>
<td>0.00</td>
<td>25.3 ± 0.4$^g$</td>
<td>31.3 ± 0.5$^g$</td>
<td>31.3 ± 0.5$^g$</td>
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<tr>
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<td>77.8 ± 1.0</td>
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<td>82.5 ± 0.6</td>
<td>85.6</td>
</tr>
</tbody>
</table>

$^a$[PSH]$_0$ = 0.2 mM, [Pip] = 0.1 M, [NaOH] = 0.03 M, λ = 370 nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. $^b$Total concentration of NaBr. $^c$Total concentration of CTABr. $^d$Total concentration of C$_{16}$E$_{20}$. $^e$Observed pseudo first order rate constant. $^f$Pseudo first order rate constant calculated from Eq. 3.13 with parameters listed in Table 3.5, $\theta = F_{X/S} k_{obs}^w$ and $K_{X/S} = K_{X/S} / (1 + K_{X/S}[CTABr]_T)$. $^g$Error limits are standard deviations.
Table 3.2: Pseudo-first-order rate constants ($k_{obs}$) for the reaction of piperidine with anionic phenyl salicylate ($PS^-$) at 0.010 M CTABr in the presence of 0.006, 0.010 and 0.015 M $C_{16}E_{20}$ and different [MX] (= NaBr).\textsuperscript{a}

<table>
<thead>
<tr>
<th>[MX]\textsuperscript{b} (M)</th>
<th>[CTABr]\textsuperscript{c} = 0.010 M</th>
<th>[CTABr]\textsuperscript{d} = 0.006 M</th>
<th>[CTABr]\textsuperscript{d} = 0.010 M</th>
<th>[CTABr]\textsuperscript{d} = 0.015 M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^4 m_{Kobs} e S^{-1}$</td>
<td>$10^4 m_{Kcalcd} f S^{-1}$</td>
<td>$10^4 m_{Kobs} e S^{-1}$</td>
<td>$10^4 m_{Kcalcd} f S^{-1}$</td>
</tr>
<tr>
<td>0.00</td>
<td>23.0 ± 0.4\textsuperscript{g}</td>
<td>17.5 ± 0.4\textsuperscript{g}</td>
<td>28.7 ± 0.3\textsuperscript{g}</td>
<td>29.0</td>
</tr>
<tr>
<td>0.01</td>
<td>24.2 ± 0.4</td>
<td>18.1 ± 0.7</td>
<td>29.4 ± 0.2</td>
<td>31.1</td>
</tr>
<tr>
<td>0.03</td>
<td>26.3 ± 0.6</td>
<td>20.1 ± 0.3</td>
<td>30.8 ± 0.4</td>
<td>34.0</td>
</tr>
<tr>
<td>0.06</td>
<td>29.8 ± 0.5</td>
<td>22.8 ± 0.6</td>
<td>34.0 ± 0.4</td>
<td>34.0</td>
</tr>
<tr>
<td>0.10</td>
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<td>26.8 ± 0.4</td>
<td>26.8 ± 0.4</td>
<td>37.6</td>
</tr>
<tr>
<td>0.12</td>
<td>34.7 ± 0.5</td>
<td>28.4 ± 0.3</td>
<td>38.1 ± 0.3</td>
<td>39.2</td>
</tr>
<tr>
<td>0.15</td>
<td>36.5 ± 0.5</td>
<td>30.3 ± 0.5</td>
<td>38.8 ± 0.5</td>
<td>41.4</td>
</tr>
<tr>
<td>0.18</td>
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</tr>
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<td>44.6 ± 0.4</td>
<td>44.6</td>
</tr>
<tr>
<td>0.25</td>
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<td>33.6 ± 0.4</td>
<td>48.2 ± 0.3</td>
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</tr>
<tr>
<td>0.30</td>
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<td>35.6 ± 0.6</td>
<td>49.5 ± 0.3</td>
<td>50.0</td>
</tr>
<tr>
<td>0.35</td>
<td>46.4 ± 0.5</td>
<td>37.3 ± 0.5</td>
<td>51.6 ± 0.5</td>
<td>52.2</td>
</tr>
<tr>
<td>0.40</td>
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<td>37.7 ± 0.4</td>
<td>54.4 ± 0.3</td>
<td>54.2</td>
</tr>
<tr>
<td>0.50</td>
<td>50.4 ± 0.5</td>
<td>40.4 ± 0.4</td>
<td>57.7 ± 0.4</td>
<td>57.6</td>
</tr>
<tr>
<td>0.60</td>
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<td>41.4 ± 0.4</td>
<td>59.5 ± 0.5</td>
<td>60.4</td>
</tr>
<tr>
<td>0.70</td>
<td>52.5 ± 0.6</td>
<td>43.3 ± 0.5</td>
<td>62.6 ± 0.2</td>
<td>62.8</td>
</tr>
</tbody>
</table>

Footnotes a, b, c, d, e, f, and g are the same as in Table 3.1.
Table 3.3: Pseudo-first-order rate constants ($k_{obs}$) for the reaction of piperidine with anionic phenyl salicylate (PS$^-$) at 0.015 M CTABr in the presence of 0.006, 0.010 and 0.015 M C$_{16}$E$_{20}$ and different [MX] (= NaBr).$^a$

<table>
<thead>
<tr>
<th>[MX]$^b$ (M)</th>
<th>[CTABr]$_f$ = 0.015 M</th>
<th>0.015 M</th>
<th>0.010 M</th>
<th>0.015 M</th>
<th>0.015 M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[C$<em>{16}$E$</em>{20}$]$_d$ = 0.006 M</td>
<td>$10^4$ $k_{obs}$ S$^{-1}$</td>
<td>$10^4$ $k_{calcd}$ S$^{-1}$</td>
<td>$10^4$ $k_{obs}$ S$^{-1}$</td>
<td>$10^4$ $k_{calcd}$ S$^{-1}$</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>21.8 ± 0.3$^e$</td>
<td>17.9 ± 0.4$^g$</td>
<td>23.22 ± 0.4$^g$</td>
<td>24.18 ± 0.4</td>
</tr>
<tr>
<td>0.01</td>
<td></td>
<td>22.4 ± 0.4</td>
<td>22.0</td>
<td>18.4 ± 0.5</td>
<td>18.0</td>
</tr>
<tr>
<td>0.03</td>
<td></td>
<td>23.9 ± 0.4</td>
<td>23.9</td>
<td>20.1 ± 0.5</td>
<td>19.4</td>
</tr>
<tr>
<td>0.06</td>
<td></td>
<td>26.1 ± 0.3</td>
<td>26.2</td>
<td>20.8 ± 0.6</td>
<td>21.4</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
<td>28.8 ± 0.4</td>
<td>28.7</td>
<td>23.8 ± 0.5</td>
<td>23.6</td>
</tr>
<tr>
<td>0.12</td>
<td></td>
<td>30.3 ± 0.2</td>
<td>29.7</td>
<td>24.9 ± 0.5</td>
<td>24.6</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>30.9 ± 0.3</td>
<td>31.1</td>
<td>26.3 ± 0.6</td>
<td>26.0</td>
</tr>
<tr>
<td>0.18</td>
<td></td>
<td>31.8 ± 0.3</td>
<td>32.3</td>
<td>26.8 ± 0.7</td>
<td>27.3</td>
</tr>
<tr>
<td>0.20</td>
<td></td>
<td>33.1 ± 0.6</td>
<td>33.0</td>
<td>28.2 ± 0.4</td>
<td>28.1</td>
</tr>
<tr>
<td>0.25</td>
<td></td>
<td>34.2 ± 0.6</td>
<td>34.5</td>
<td>29.1 ± 0.5</td>
<td>29.9</td>
</tr>
<tr>
<td>0.30</td>
<td></td>
<td>35.7 ± 0.8</td>
<td>35.8</td>
<td>30.5 ± 0.5</td>
<td>31.4</td>
</tr>
<tr>
<td>0.35</td>
<td></td>
<td>37.3 ± 0.6</td>
<td>36.8</td>
<td>33.2 ± 0.4</td>
<td>32.8</td>
</tr>
<tr>
<td>0.40</td>
<td></td>
<td>38.5 ± 0.6</td>
<td>37.7</td>
<td>34.1 ± 0.2</td>
<td>34.0</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td>38.9 ± 0.7</td>
<td>39.1</td>
<td>35.8 ± 0.3</td>
<td>36.1</td>
</tr>
<tr>
<td>0.60</td>
<td></td>
<td>39.5 ± 0.8</td>
<td>40.2</td>
<td>37.9 ± 0.6</td>
<td>37.7</td>
</tr>
<tr>
<td>0.70</td>
<td></td>
<td>40.7 ± 0.8</td>
<td>41.0</td>
<td>38.8 ± 0.5</td>
<td>39.1</td>
</tr>
</tbody>
</table>

Footnotes $a$, $b$, $c$, $d$, $e$, $f$ and $g$ are the same as in Table 3.1.
**Figure 3.1:** Plot of $k_{obs}$ against $[2-\text{NaOC}_6\text{H}_4\text{CO}_2\text{Na}]$ for the piperidinolysis of $\text{PS}^-$ at 35 °C in the presence of $[\text{CTABr}]_T/M = 0.006$ (●), 0.010 (♦) and 0.015 (▲). The solid curves are sketched via the calculated values of the rate constant ($k_{calcd}$). Insert: The plots at magnified scale for the data points at lower values of $[M_2X]$.

**Figure 3.2:** Plots of $^{m}k_{obs}$ (where superscript “m” represents mixed micelles) against $[2-\text{NaOC}_6\text{H}_4\text{CO}_2\text{Na}]$ for the piperidinolysis of $\text{PS}^-$ at $[\text{CTABr}]_T + [\text{C}_{16}\text{E}_{20}]_T/M = 0.006 + 0.006$ (●), 0.006 + 0.010 (♦) and 0.006 + 0.015 (▲) and 35 °C. The solid curves represent the calculated values of rate constant ($k_{calcd}$). Insert: The enlarged plots for the concentrations of $M_2X$ at lower values.
Figure 3.3: Plots of $^{m}k_{obs}$ (where superscript “m” represents mixed micelles) against [2-NaOC₆H₄CO₂Na] for the piperidolysis of PS⁻ at [CTABr]₁ + [C₁₆E₂₀]₁/M = 0.010 + 0.006 (●), 0.010 + 0.010 (♦) and 0.010 + 0.015 (▲) and 35 °C. The solid curves are sketched via the calculated values of rate constant ($k_{calcd}$). Insert: The enlarged plots for the concentrations of M₂X at lower values.

Figure 3.4: Plots of $^{m}k_{obs}$ (where superscript “m” represents mixed micelles) against [2-NaOC₆H₄CO₂Na] for the piperidolysis of PS⁻ at [CTABr]₁ + [C₁₆E₂₀]₁/M = 0.015 + 0.006 (●), 0.015 + 0.010 (♦) and 0.015 + 0.015 (▲) and 35 °C. The solid curves are sketched via the calculated values of rate constant ($k_{calcd}$). Insert: The enlarged plots for the concentrations of M₂X at lower values.
Figure 3.5: Graphs of shear viscosity (\(\eta\)) against shear rates (\(\dot{\gamma}\)) for the piperidinolysis of PS\(^-\) containing 0.015 M CTABr and \([2-NaOC_6H_4CO_2Na]/M = (a) 0.006 (\bullet) 0.008 (\Box) 0.012 (\blacktriangle) 0.020 (\blacktriangledown) 0.040 (\circ) 0.08 (\blacklozenge) and 0.120 (\blacksquare) at 25 °C and (b) 0.006 (\bullet) 0.008 (\Box) 0.012 (\blacktriangle) 0.020 (\blacktriangledown) 0.040 (\circ) 0.080 (\blacklozenge) and 0.120 (\blacksquare) at 35 °C.
Figure 3.6: Plots of shear viscosity (\( \eta \)) against shear rate (\( \dot{\gamma} \)) for the piperidinolysis of PS\(^-\) containing 0.015 M CTABr, 0.006 M C\(_{16}E_{20}\) and [2-NaOC\(_6H_4CO_2\)Na]/M = (a) 0.006 (*) 0.008 (\( \square \)) 0.0120 (\( \blacktriangle \)) 0.020 (\( \bullet \)) 0.040 (\( \circ \)) and 0.120 (\( \heartsuit \)) at 25 °C and (b) 0.006 (*) 0.008 (\( \square \)) 0.0120 (\( \blacktriangle \)) 0.020 (\( \bullet \)) 0.040 (\( \circ \)) and 0.120 (\( \heartsuit \)) at 35 °C.
3.4 Discussion

3.4.1 Explanation of kinetic observations for the piperidinolysis of PS$^-$ in the presence of pure C$_{16}$E$_{20}$ micelles at various [MX] or [M$_2$X] and 35 ºC

The data obtained revealed that the values of $k_{\text{obs}}$ at various values of [MX] (MX = NaBr) or [M$_2$X] (M$_2$X = 2-NaOC$_6$H$_4$CO$_2$Na) = 0 (or average of higher values of $k_{\text{obs}}$ ($k_{\text{obs}}^0$)) and those of $k_{\text{obs}}$ at maximum value [MX] or [M$_2$X] ($k_{\text{obs}}^{\text{MX (max)}}$ or $k_{\text{obs}}^{\text{M}_2\text{X (max)}}$), decrease with the increase in [C$_{16}$E$_{20}$]$_T$ ([C$_{16}$E$_{20}$]$_T$ = 0.001, 0.003, 0.006, 0.008, 0.010 or 0.015 M). These are similar to the reported results in the past (Khan & Ismail, 2004). The presence of C$_{16}$E$_{20}$ shows a negative salt effect (NSE) and the values of $k_{\text{obs}}^0$ and $k_{\text{obs}}^{\text{MX (max)}}$ were used to calculate the percent negative salt effect (%NSE); values presented in Table 3.4, using Eq. 3.12. These values were found to decrease with the increase in [C$_{16}$E$_{20}$]$_T$.

$$\text{%NSE} = \left( \frac{k_{\text{obs}}^0 - k_{\text{obs}}^{\text{MX (max)}}}{k_{\text{obs}}^0} \right) \times 100$$

or

$$\text{%NSE} = \left( \frac{k_{\text{obs}}^0 - k_{\text{obs}}^{\text{M}_2\text{X (max)}}}{k_{\text{obs}}^0} \right) \times 100 \quad (3.12)$$

where $k_{\text{obs}}^0 = k_{\text{obs}}$ at [MX] or [M$_2$X] = 0 (or average values of higher values of $k_{\text{obs}}$) and $k_{\text{obs}}^{\text{MX (max)}}$ or $k_{\text{obs}}^{\text{M}_2\text{X (max)}} = k_{\text{obs}}$ at the maximum value of [MX] or [M$_2$X].
3.4.2 Explanation of kinetic observations for the piperidinolysis of PS− in the presence of pure CTABr and mixed CTABr-C\textsubscript{16}E\textsubscript{20} micelles at various [MX] or [M\textsubscript{2}X] and 35 °C

The values of \(k_{obs}\) obtained in the presence of a constant concentration of pure CTABr at various [MX] or [M\textsubscript{2}X] (where M\textsubscript{2}X = 2-NaOC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}Na) were related to Eq. 3.13 (Khan et al., 2010).

\[
k_{obs} = \frac{k_{0} + \theta K^{X/S}([MX] - [MX]_{0}^{op})}{1 + K^{X/S}([MX] - [MX]_{0}^{op})}
\]

or

\[
k_{obs} = \frac{k_{0} + \theta K^{X/S}([M_{2}X] - [M_{2}X]_{0}^{op})}{1 + K^{X/S}([M_{2}X] - [M_{2}X]_{0}^{op})}
\]

where \(k_{0}\) stands for \(k_{obs}\) in the absence of MX or M\textsubscript{2}X with, respectively, [MX]\textsubscript{0}\textsuperscript{op} or [M\textsubscript{2}X]\textsubscript{0}\textsuperscript{op} (represent the optimum values of [MX] (= NaBr) or [M\textsubscript{2}X] at which further increase in [MX] or [M\textsubscript{2}X] is believed to have no effect on ion exchange X\textsuperscript−/HO\textsuperscript− and X\textsuperscript−/Br\textsuperscript− occurring in the CTABr micellar phase) (Khan, 2010). The values of [MX]\textsubscript{0}\textsuperscript{op} or [M\textsubscript{2}X]\textsubscript{0}\textsuperscript{op}, at various [CTABr]\textsuperscript{T}, were determined by an iterative technique as described in detail in the previously published reports (Khan & Ismail, 2003; Khan & Ismail, 2009). Parameters \(\theta\) and \(K^{X/S}\) represent the empirical constants and their values were calculated from Eq. 3.13 using nonlinear least-squares relationship, considering \(k_{0}\) to have known value. Different \(k_{0}\) (= \(k_{obs}\) at [MX] = [MX]\textsubscript{0}\textsuperscript{op} = 0 or [M\textsubscript{2}X] = [M\textsubscript{2}X]\textsubscript{0}\textsuperscript{op} = 0) were determined by conducting kinetic experiments at typical [CTABr]\textsuperscript{T} as well as [CTABr]\textsuperscript{T} + [C\textsubscript{16}E\textsubscript{20}]\textsuperscript{T} and their values are shown in Tables 3.1, 3.2 and 3.3.
Table 3.4: Values of kinetic parameters for the reaction of Pip and PS\(^-\) in the presence of inert salts MX or M\(_2\)X at different \([C_{16}E_{20}]_T\) and 35 °C.\(^a\)

<table>
<thead>
<tr>
<th>([C_{16}E_{20}]_T ) M</th>
<th>(k_{obs}^0 ) S(^{-1})</th>
<th>(k_{obs}^{MX (max)} ) S(^{-1})</th>
<th>% NSE(^e)</th>
<th>(k_{obs}^0 ) S(^{-1})</th>
<th>(k_{obs}^{M_2X (max)} ) S(^{-1})</th>
<th>% NSE(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>279</td>
<td>193</td>
<td>31</td>
<td>276</td>
<td>177</td>
<td>36</td>
</tr>
<tr>
<td>0.003</td>
<td>254</td>
<td>188</td>
<td>26</td>
<td>254</td>
<td>204</td>
<td>20</td>
</tr>
<tr>
<td>0.006</td>
<td>227</td>
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<td>229</td>
<td>204</td>
<td>11</td>
</tr>
<tr>
<td>0.008</td>
<td>210</td>
<td>176</td>
<td>16</td>
<td>173</td>
<td>166</td>
<td>4.0</td>
</tr>
<tr>
<td>0.010</td>
<td>191</td>
<td>173</td>
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<td>276</td>
<td>177</td>
<td>36</td>
</tr>
<tr>
<td>0.015</td>
<td>177</td>
<td>165</td>
<td>07</td>
<td>239</td>
<td>202</td>
<td>14</td>
</tr>
</tbody>
</table>

\(^a\)[PSH]\(_0\) = 0.20 mM, [NaOH] = 0.03 M, [Pip] = 0.10 M, \(\lambda = 370\) nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. \(^b\)Total concentration of \(C_{16}E_{20}\). \(^c\)\(k_{obs}^0\) = \(k_{obs}\) at [MX] or [M\(_2\)X] = 0 (or average value of similar values of \(k_{obs}\) at various [MX] or [M\(_2\)X]). \(^d\)\(k_{obs}^{MX (max)}\) or \(k_{obs}^{M_2X (max)}\) = \(k_{obs}\) at maximum value of [MX] or [M\(_2\)X]. \(^e\)Percent negative salt effect, %NSE calculated from Eq. 3.12.
The values of \( k_{\text{obs}} \) obtained in the presence of mixed CTABr-C16E20 micelles within the concentration range of 0.006-0.015 M C16E20 surfactants were also found to fit to Eq. 3.13. The values of fraction of micellized S ion transferred from the CTABr micellar phase to aqueous phase, through the occurrence of ion exchange \( S^-/PS^- \), is denoted as \( F_{X/S} \). The relationship between \( \theta \) and \( F_{X/S} \) is expressed in Eq. 3.14.

\[
\theta = F_{X/S} k_{\text{obs}}^W
\]  

(3.14)

where \( k_{\text{obs}}^W = k_{\text{obs}}^2 \) denotes \( k_{\text{obs}} \) at different \([\text{C}16\text{E}20]_T = 0.006, 0.010 \) and 0.015 M) and \([\text{MX}]\) or \([\text{M}_2\text{X}] = [\text{CTABr}] = 0 \) with \( k_{\text{W}}^2 \) representing the nucleophilic second order rate constant in nonionic C16E20 micellar phase. The values of \( K_{X/S} \), presented in Tables 3.5, 3.6 and 3.7, at various concentrations of pure CTABr micelles as well as mixed CTABr-C16E20 micelles, were determined by the use of Eq. 3.13 (Khan & Arifin, 1996). The values of \( K_{X/S} \), obtained for pure CTABr micelles (Table 3.6), were calculated from Eq. 3.15 with the value of \( K_{S}^0 \) as 7000 M\(^{-1} \) obtained from the literature (Khan & Arifin, 1996).

\[
K_{X/S} = K_{X/S}^0 \left( 1 + K_{S}^0 [\text{CTABr}]_T \right)
\]  

(3.15)

The results obtained at various constant concentrations of pure CTABr and mixed CTABr-C16E20, in the presence of different [MX] and [M2X] (MX= NaBr and M2X = NaOC6H4CO2Na), are presented in Tables 3.5, 3.6 and 3.7. Symbolic modification of parameters was done to differentiate between those obtained in the presence of pure micelles and mixed micelles. Therefore, \( k_{\text{obs}} \), \( k_0 \), \( k_{\text{obs}}^W \), \( k_{\text{W}}^2 \), \( \theta \), \( K_{X/S} \), \( K_{S}^0 \), \( F_{X/S} \) and \( K_{X/S}^n \) are considered as \( m^{k_{\text{obs}}} \), \( m^{k_0} \), \( m^{k_{\text{obs}}^W} \), \( m^{k_{W}} \), \( m^\theta \), \( m^{K_{X/S}} \), \( m^{K_{S}^0} \), \( m^{F_{X/S}} \) and \( m^{K_{X/S}^n} \). The small letter “m” (superscript) was used to imply that the parameters obtained in the of mixed micellar solutions throughout the text.
The values of $k_{\text{obs}}$, in the presence of 0.006, 0.010 and 0.015 M pure CTABr, at various [2-HOC$_6$H$_4$CO$_2$Na] (Figure 3.1) has been observed to decrease with the increase in total concentration of CTABr. The understandings of the complex headgroups for C$_{16}$E$_{20}$ micelles with regards to the change in its structure have not yet been reported. The hydrophilic parts of CTABr in CTABr-C$_{16}$E$_{20}$ surfactants mixture are covered within the larger sized hydrophilic C$_{16}$E$_{20}$ micellar parts of the same mixed surfactants (Gao et al., 2002). Thus, it appears acceptable that the combination of ionic surfactants (C$_n$IM) and nonionic ones (C$_n$Em) with $n \leq m$ is related to incomplete dehydration of hydrophilic part of C$_n$IM (comprising the outermost portion of headgroups) which causes the ion exchange, leading to changes in structure of micelles from spherical to wormlike (Geng et al., 2006).

It is clearly demonstrated from Eq. 3.15 that as the concentration of pure CTABr increases, the values of $K_X/S$ decrease provided the values of $K_X/S$ are independent of [CTABr]$_T$. This prediction coincides well with what is presented in Table 3.6 (the values of $K_X/S = 39, 26$ and $13$ for 0.006, 0.010 and 0.015 M CTABr, respectively).

The optimum values of [2-NaOC$_6$H$_4$CO$_2$Na], ([M$_2$X]$^0_0$), for the mixed CTABr-C$_{16}$E$_{20}$ micelles (Table 3.7) decreased compared to that of the pure CTABr (Table 3.6). But the values of parameters $k_0$, $\theta$ and $K_X/S$ remain independent of whether the micellar system is pure or mixed, and it was observed that the lowest value of the concentration of CTABr is more than 20-fold larger than the corresponding value of [M$_2$X]$^0_0$ (Table 3.7) in the presence of 0.006 M C$_{16}$E$_{20}$.

The magnitude of normalised values of $K_X/S$ ($K_{X/S}^n = F_X/S K_X/S$) is related to values of cationic micellar binding constants, $K_X$ (for counterion X), and $K_S$, (for counterion S with $S^- = \text{PS}^-$) with the relationship; $K_{X/S}^n = \Omega_S K_X/K_S$ where $\Omega_S$ is denoting a proportionality constant (Khan, 2010). Similarly, for another ion exchange (with the reference counterion
Br−) Br/S, the magnitude of normalised values of $K_{Br/S}$ ($K_{Br/S}^n = F_{Br/S}/K_{Br/S}$) has the relationship; $K_{Br/S}^n = \Omega_S K_B/K_S$ (Khan, 2010). The values of $K_{X/S}^n$, summarised in Table 3.6, and the reported value of $K_{Br/S}^n (= 25 \text{ M}^{-1})$ (Khan, 1997a; Khan et al., 2000; Khan & Ismail, 2007) were used to calculate the values of conventional ion exchange constant/relative counterion binding constants, $K_{Br}^X$, using Eq. 3.16. The values of $K_{Br}^X$ (presented in Table 3.6) are 48.8, 45.0 and 33.1 at, respectively, [CTABr]$_T = 0.006$, 0.010 and 0.015 M. These results are relatively more reliable as the mean value of $K_{Br}^X (= 42)$ is similar to the one presented in the previous study ($K_{Br}^X = 44$) (Khan et al., 2010).

$$K_{Br}^X = K_X/K_B = K_{X/S}^n/K_{Br/S}^n$$

(3.16)

Eq. 3.16 holds only if the values of $K_{X/S}^n$ and $K_{Br/S}^n$ are determined in the presence of micelles with the same structural behavior/feature (such as spherical or wormlike micelles or vesicles). However, if the values of $K_{X/S}^n$ and $K_{Br/S}^n$ have been determined in the presence of respective nonspherical and spherical micelles, then $K_{Br}^X$ should represent $R_{Br}^X$ (= $K_{X}^{nsp}/K_{Br}^{sp}$ with $K_{X}^{nsp}$ and $K_{Br}^{sp}$ representing non-spherical and spherical micellar binding constants of X− and Br−, respectively) with the relationship represented by Eq. 3.17

$$R_{Br}^X = (nK_{X/S}^{nsp})/(nK_{Br/S}^{sp})$$

(3.17)

The conditions to use either of the relationships (Eqs. 3.16 and 3.17) have been reported in detail in the previous report (Khan et al., 2010). It is perhaps noteworthy that Eqs. 3.16 and 3.17 are applicable for both $M_2X (= 2-\text{NaOC}_6\text{H}_4\text{CO}_2\text{Na})$ and $MX (= \text{NaBr})$.

The observed data ($mK_{obs}$ versus [MX] with superscript “m” representing mixed micelles) obtained in mixed micelles, CTABr-C$_{16}$E$_{20}$, were found to follow Eq. 3.13 which is also applicable for observed data obtained in the presence of pure CTABr micelles. It is therefore assumed that Eqs. 3.16 and 3.17 should be applicable for data in
the mixed micelles, CTABr-C_{16}E_{20}, with symbols $K_X^{Br}$, $K_X$, $K_{Br}$, $K_{X/S}$, $K_{Br/S}$, $R_X^{Br}$, ($^{n}K_X/S$)$^{sp}$ and ($^{m}K_{Br/S}$)$^{sp}$ replaced by respective $^{m}K_X^{Br}$, $^{m}K_X$, $^{m}K_{Br}$, $^{m}K_{X/S}$, $^{m}K_{Br/S}$, $^{m}R_X^{Br}$, ($^{m}K_{X/S}$)$^{sp}$ and ($^{m}K_{Br/S}$)$^{sp}$. The values of $^{m}K_{X/S}$ and $^{m}K_{Br/S}$ could not be calculated because the values of $K_S^0$ for mixed CTABr-C_{16}E_{20} surfactants are not available for the present study. Consequently, the values of $^{m}K_{X/S}$, $^{m}K_{Br/S}$, ($^{m}K_{X/S}$)$^{sp}$ and ($^{m}K_{Br/S}$)$^{sp}$ could not be calculated. In this case, Eq. 3.16 or 3.17 could not be applied in determining the respective values of $^{m}K_X^{Br}$ or $^{m}R_X^{Br}$.

However, it can be easily shown, in view of Eq. 3.15, that

$$m^{K_{X/S}}_{X} = m^{n}K_{X/S} (1 + m^{K_{S}^0}_{CTABr} r) \quad (3.18)$$

and

$$m^{K_{Br/S}}_{Br} = m^{n}K_{Br/S} (1 + m^{K_{S}^0}_{CTABr} r) \quad (3.19)$$

The relationships in Eqs. 3.18 and 3.19 give Eq. 3.20.

$$m^{K_X}^{Br} = \frac{m^{n}K_{X/S}}{m^{n}K_{Br/S}} \quad (3.20)$$

with $^{m}K_{X/S} = m^{F_{X/S}}^{m}K_{X/S}$ and $^{m}K_{Br/S} = m^{F_{Br/S}}^{m}K_{Br/S}$. 


Table 3.5: Values of empirical constants, $m_0$, $m_{F/S}$ and $m_{K/X/S}$ calculated from Eqs. 3.13 and 3.14 for MX = NaBr at different concentrations of mixed CTABr-C$_{16}$E$_{20}$.

<table>
<thead>
<tr>
<th>[CTABr]$_T$</th>
<th>[C$<em>{16}$E$</em>{20}$]$_T$</th>
<th>$10^4 m_k^d$</th>
<th>$10^3 m_0$</th>
<th>$m_{K/X/S}$</th>
<th>$m_{F/X/S}$</th>
<th>$m_{n_{K/X/S}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M</td>
<td>s$^{-1}$</td>
<td>s$^{-1}$</td>
<td>M$^{-1}$</td>
<td></td>
<td>M$^{-1}$</td>
</tr>
<tr>
<td>0.006$^b$</td>
<td>0.006$^c$</td>
<td>25.3 ± 0.4$^e$</td>
<td>10.1 ± 0.3$^e$</td>
<td>3.4 ± 0.3$^e$</td>
<td>0.4$^f$</td>
<td>1.4$^f$</td>
</tr>
<tr>
<td>0.006</td>
<td>0.010</td>
<td>31.3 ± 0.5$^f$</td>
<td>10.3 ± 0.9$^f$</td>
<td>4.4 ± 0.8$^f$</td>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>0.006</td>
<td>0.015</td>
<td>30.1 ± 0.3</td>
<td>11.4 ± 0.6$^g$</td>
<td>3.0 ± 0.4$^g$</td>
<td>0.6</td>
<td>1.8</td>
</tr>
<tr>
<td>0.010</td>
<td>0.006</td>
<td>23.0 ± 0.4$^g$</td>
<td>6.6 ± 0.1$^g$</td>
<td>3.2 ± 0.1$^g$</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>17.5 ± 0.4$^g$</td>
<td>5.2 ± 0.6$^g$</td>
<td>3.7 ± 0.1$^g$</td>
<td>0.3</td>
<td>1.1</td>
</tr>
<tr>
<td>0.010</td>
<td>0.015</td>
<td>28.7 ± 0.3$^g$</td>
<td>8.5 ± 0.1$^g$</td>
<td>1.8 ± 0.7$^g$</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>0.015</td>
<td>0.006</td>
<td>21.8 ± 0.3$^g$</td>
<td>4.8 ± 0.1$^g$</td>
<td>3.8 ± 0.2$^g$</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>0.015</td>
<td>0.010</td>
<td>17.9 ± 0.4$^g$</td>
<td>5.4 ± 0.1$^g$</td>
<td>2.1 ± 0.1$^g$</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
<td>23.2 ± 0.4$^g$</td>
<td>5.9 ± 0.2$^g$</td>
<td>2.6 ± 0.2$^g$</td>
<td>0.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

$^a[PSH]_0 = 0.2$ mM, [Pip] = 0.1 M, [NaOH] = 0.03 M, $\lambda = 370$ nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. $^b$Total concentration of CTABr. $^c$Total concentration of C$_{16}$E$_{20}$. $^d m_k = m_{k_{obs}}$ at [MX] = [MX]$_0$. $^e$Error limits are standard deviations. $^f m_{F/X/S} = m_0 m_{W_{obs}}^{-1}$; with $m_{W_{obs}}^{-1} = m_{k_{obs}} (= m_k^2 [Pip]_T)$ = 240 x 10$^{-4}$, 193.2 x 10$^{-4}$ and 184.2 x 10$^{-4}$ s$^{-1}$ at constant [C$_{16}$E$_{20}$]$_T$ (0.006, 0.010 and 0.015 M [C$_{16}$E$_{20}$] respectively) and [MX] = [CTABr] = 0. $^g m_{n_{K/X/S}} = m_{F/X/S} m_{K/X/S}$. 
Table 3.6: Values of empirical constants, 0, $F_{X/S}$ and $K_{X/S}$ obtained using Eqs. 3.13 and 3.14 with the $[M_2X]_0^{op}$ values for $M_2X = 2\text{NaOC}_6\text{H}_4\text{CO}_2\text{Na}$ at different $[\text{CTABr}]_T$. $^a$

<table>
<thead>
<tr>
<th>$[\text{CTABr}]_T \text{M}$</th>
<th>$10^4 k_0^{e} \text{s}^{-1}$</th>
<th>$[M_2X]_0^{op} \text{M}$</th>
<th>$10^3 \theta \text{s}^{-1}$</th>
<th>$K_{X/S} \text{M}^{-1}$</th>
<th>$K_{X/S} \text{M}^{-1}$</th>
<th>$F_{X/S}$</th>
<th>$K_{X/S}^{n} \text{M}^{-1}$</th>
<th>$K_{X}^{\text{Br or R}_{X}^{\text{Br}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006 $^b$</td>
<td>23.0 ± 0.2 $^d$</td>
<td>0.007</td>
<td>23.1 ± 0.1 $^d$</td>
<td>39.4 ± 5.6 $^d$</td>
<td>1694.2 $^e$</td>
<td>0.72 $^f$</td>
<td>1219.8 $^e$</td>
<td>48.8 $^h$</td>
</tr>
<tr>
<td>0.010</td>
<td>21.2 ± 0.4</td>
<td>0.011</td>
<td>19.4 ± 0.6</td>
<td>26.4 ± 2.4</td>
<td>1874.4</td>
<td>0.60</td>
<td>1124.6</td>
<td>45.0</td>
</tr>
<tr>
<td>0.015</td>
<td>16.4 ± 0.4</td>
<td>0.016</td>
<td>19.6 ± 0.4</td>
<td>13.0 ± 0.6</td>
<td>1378.0</td>
<td>0.60</td>
<td>0826.8</td>
<td>33.1</td>
</tr>
</tbody>
</table>

$^a$[$\text{PSH}]_0 = 0.2 \text{mM, [NaOH]} > 0.03 \text{M, [Pip]} = 0.1 \text{M, } \lambda = 370 \text{nm and aqueous reaction mixture for each kinetic run contains 2\% v/v acetonitrile. Footnote } b \text{ is the same as in Table 3.5.} $^c$k_0 = k_{obs}$ at $[MX] = [MX]_0^{op}$. $^d$Error limits are standard deviations. $^e$K_{X/S} = K^{X/S}(1 + K_0^{S} [\text{CTABr}]_T)$, where K_0^{S} = 7 x 10^3 M^{-1}. $^f$F_{X/S} = 0/(k_{W}^{2} [\text{Pip}]_T), where k_{W} = k_{obs}$ at $[\text{CTABr}]_T = [C_{16}E_{20}]_T = 0$ and $[\text{Pip}]_T = 0.1 \text{M and the values of } k_{W}^{2}$, under such conditions is 0.322 s^{-1}. $^g$K_{X/S}^{n} = F_{X/S} K_{X/S}. $^h$K_{X}^{\text{Br or R}_{X}^{\text{Br}}}$ or $R_{X}^{\text{Br}}$ = K_{X/S}^{n}/ K_{Br/S}^{n}$, where K_{Br/S}^{n} = 25 M^{-1}. 


Table 3.7: Values of empirical constants, \(m_0\), \(m_{FX/S}\) and \(m_{KX/S}\) calculated from Eqs. 3.13 and 3.14 with the \([M_2X]_0^{op}\) values for \(M_2X = 2NaOC\_6H\_4CO\_2Na\) at different concentrations of mixed CTABr-C\(_{16}E_{20}\)^a

<table>
<thead>
<tr>
<th>([\text{CTABr}]_T) M</th>
<th>([\text{C}<em>{16}E</em>{20}]) M</th>
<th>(10^4m_0^d) (\text{s}^{-1})</th>
<th>(10^3m_0) (\text{s}^{-1})</th>
<th>(m_{KX/S}) M(^{-1})</th>
<th>(m_{FX/S})</th>
<th>(m_{nKX/S}) M(^{-1})</th>
<th>(m_{nKBr/S}) M(^{-1})</th>
<th>(m_{KX}^{Br} ) or (m_{R_{X}}^{Br})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006(^b)</td>
<td>0.006(^c)</td>
<td>24.7 ± 0.5(^e)</td>
<td>0.00028</td>
<td>20.8 ± 0.4(^e)</td>
<td>34.8 ± 2.2(^e)</td>
<td>0.87(^f)</td>
<td>30.3(^g)</td>
<td>1.4(^h)</td>
</tr>
<tr>
<td>0.006</td>
<td>0.010</td>
<td>27.2 ± 0.5</td>
<td>0.00201</td>
<td>19.9 ± 0.2</td>
<td>28.1 ± 0.9</td>
<td>1.03</td>
<td>28.9</td>
<td>2.2</td>
</tr>
<tr>
<td>0.006</td>
<td>0.006</td>
<td>14.1 ± 0.1</td>
<td>0.00000</td>
<td>21.7 ± 0.5</td>
<td>24.6 ± 1.5</td>
<td>1.18</td>
<td>29.9</td>
<td>1.8</td>
</tr>
<tr>
<td>0.010</td>
<td>0.006</td>
<td>22.9 ± 0.8</td>
<td>0.00000</td>
<td>26.5 ± 0.5</td>
<td>8.82 ± 0.4</td>
<td>1.10</td>
<td>09.7</td>
<td>1.0</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>25.3 ± 0.4</td>
<td>0.00006</td>
<td>35.0 ± 1.1</td>
<td>4.87 ± 0.2</td>
<td>1.82</td>
<td>08.9</td>
<td>1.1</td>
</tr>
<tr>
<td>0.010</td>
<td>0.015</td>
<td>25.3 ± 0.5</td>
<td>0.00047</td>
<td>32.3 ± 0.5</td>
<td>7.26 ± 0.2</td>
<td>1.75</td>
<td>12.7</td>
<td>0.9</td>
</tr>
<tr>
<td>0.015</td>
<td>0.006</td>
<td>23.6 ± 0.2</td>
<td>0.01085</td>
<td>19.6 ± 0.4</td>
<td>16.8 ± 0.8</td>
<td>0.82</td>
<td>13.8</td>
<td>0.8</td>
</tr>
<tr>
<td>0.015</td>
<td>0.010</td>
<td>24.5 ± 0.3</td>
<td>0.00768</td>
<td>20.6 ± 0.4</td>
<td>16.8 ± 0.9</td>
<td>0.86</td>
<td>14.5</td>
<td>0.6</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
<td>19.9 ± 0.4</td>
<td>0.00560</td>
<td>18.0 ± 0.4</td>
<td>12.4 ± 0.6</td>
<td>0.98</td>
<td>12.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Footnote a is the same as in Table 3.6. Footnotes b, c, d, e and f are the same in Table 3.5. \(g m_{nKX/S} = \frac{m_{FX/S} m_{KX/S}}{m_{FX/S}}\), \(h m_{nKBr/S} = \frac{m_{FBr/S} m_{KBr/S}}{m_{FBr/S}}\) (for the reference salt, \(MX = NaBr\)). \(r m_{KX}^{Br}\) or \(m_{R_{X}}^{Br} = m_{nKX/S} / m_{nKBr/S}\).
The conditions to use Eq. 3.20 are also the same as in the case of Eq. 3.16. Furthermore, if the conditions fail, Eq. 3.21 should be used instead.

\[
m^n_R^{\text{Br}} = (m^n_{K^{X/S}})^{\text{sp}} / (m^n_{K^{Br/S}})^{\text{sp}}
\]

with \((m^n_{K^{X/S}})^{\text{sp}} = (m^n_{F^{X/S}})^{\text{sp}} (m^n_{K^{X/S}})^{\text{ssp}} / (m^n_{K^{Br/S}})^{\text{sp}} = (m^n_{F^{Br/S}})^{\text{sp}} (m^n_{K^{Br/S}})^{\text{sp}}\).

In general, Eqs. 3.16 and 3.20 are applicable if the values of \(K^n_{X/S}\) and \(K^n_{Br/S}\) (for pure micelles) and \(m^n_{K^{X/S}}\) and \(m^n_{K^{Br/S}}\) (for mixed micelles) are determined in the presence of micelles with the same structural behavior/feature respectively. But Eqs. 3.17 and 3.21 are applicable if the values of \(K^n_{X/S}\) and \(K^n_{Br/S}\) (for pure micelles) and \(m^n_{K^{X/S}} / m^n_{K^{Br/S}}\) (for mixed micelles) have been determined in the presence of respective nonspherical and spherical micelles.

The presence of mixed CTABr-C_{16}E_{20} micelles revealed the increase in the values of \(m^n_{F^{X/S}}\) for \(M_2X = 2\text{-NaOC}_6\text{H}_4\text{CO}_2\text{Na}\) (Table 3.6).

3.4.3 Explanation of rheological measurements for the piperidinolysis of PS^- in the presence of pure CTABr and mixed CTABr-C_{16}E_{20} micelles at various [M_2X]

In the presence pure CTABr micelles, all flow curves in Figures 3.5 (a) and (b) at \(\geq 0.012\) M 2-NaOC\(_6\)H\(_4\)CO\(_2\)Na and at both, 25 and 35 °C show the Newtonian fluid behavior at their beginning with the exception of 0.006 and 0.008 M 2-NaOC\(_6\)H\(_4\)CO\(_2\)Na while showing the shear thinning behavior at the end. This behavior of CTABr surfactant, with a constant concentration in the presence of different [2-NaOC\(_6\)H\(_4\)CO\(_2\)Na], indicates the possible presence of elongated micelles (Lu et al., 2008; Qiao et al., 2011). As the [2-NaOC\(_6\)H\(_4\)CO\(_2\)Na] increases from 0.006 to 0.012 M, the values of critical shear rate (\(\gamma_{cr}\)) decrease and also shift to lower values with increase in zero shear viscosity (\(\eta_0\)). This critical shear rate is the specific shear rate at which the values of shear viscosity (\(\eta\)) begin
to decrease (shear thinning). However, further increase in [2-NaOC₆H₄CO₂Na] (0.02-0.12 M) increases the values of \( \gamma_{ct} \) with a decrease in \( \eta_0 \). It implies, therefore, the CTABr micellar structure is getting networked to a great extent, and to a lesser degree at > 0.008 to 0.012 M and 0.02 to 0.12 M range of 2-NaOC₆H₄CO₂Na respectively. This is a typical rheological behavior of wormlike micelles (Yusof & Khan, 2013; Yusof et al., 2013). Almost all of the flow curves in Figures 3.6 (a) and (b) (0.006-0.12 M 2-NaOC₆H₄CO₂Na) at 25 and 35 °C, in the presence of mixed CTABr-C₁₆E₂₀ (with fixed concentration of both CTABr-C₁₆E₂₀), show Newtonian fluid systems.

The graphs of \( \eta_0 \) at constant shear rate (\( \dot{\gamma} \)) against [2-HOC₆H₄CO₂Na] at both 25 and 35 °C are shown in Figure 3.7. Typical single asymmetrical maxima at [CTABr] = 0.015 M, [C₁₆E₂₀] = 0, and 25 and 35 °C (represented by respectively □ and ◊ in Figure 3.7) were obtained at the same value of [2-HOC₆H₄CO₂Na]ₚ = (0.02 M). The values of specific concentration of 2-HOC₆H₄CO₂Na, [2-HOC₆H₄CO₂Na]ₚ, at which the viscosity maximum occurs at a constant \( \dot{\gamma} \), [CTABr], and both 25 and 35 °C remained unchanged. This observation agreed with previously reported studies (Abdel-Rahem, 2008; Davies et al., 2006) where the maxima obtained at fixed concentration of cationic surfactant in solution and various [MX] (where MX stands for counterionic salt) reveals the possibility of the existence of wormlike micelles. Despite the fact that the presence of, at least, single maximum in such a plot is no longer unusual (Abdel-Rahem, 2008; Ali & Makhloufi, 1999; Davies et al., 2006; Dreiss, 2007; Lin et al., 2009; Oelschlaeger et al., 2008; Rehage & Hoffmann, 1991; Schubert et al., 2004), the molecular mechanism for the cause of such a maximum is still not fully understood even at a fundamental molecular level (Davies et al., 2006; Ziserman et al., 2009). However, it has turned out to be practically certain from several studies (Abdel-Rahem, 2008; Ali & Makhloufi, 1999; Davies et al., 2006; Dreiss, 2007; Lin et al., 2009; Oelschlaeger et al., 2008; Rehage & Hoffmann, 1991; Schubert et al., 2004) that the occurrence of a viscosity maximum for a surfactant solution containing
a constant concentration of ionic micelle-forming surfactant and various concentration of counterionic salt is characteristic of the presence of WM/entangled WM in the surfactant solutions. In mixed CTABr-C₁₆E₂₀ micellar solution at 0.015 M CTABr, 0.006M C₁₆E₂₀ and 25 and 35 °C (represented by respectively △ and ○ in Figure 3.7) however, no maxima were obtained. Hence, no significant changes in the respective values of shear viscosity at different values of [2-HOC₆H₄CO₂Na]sp were noticed.

![Graph](image)

**Figure 3.7**: Graphs of zero shear viscosity (η₀) at a constant shear rate (γ̇) against [2-HOC₆H₄CO₂Na] with 0.015 M CTABr in absence of C₁₆E₂₀ at 25°C (□) and 35 °C (◊), and presence of 0.006 M C₁₆E₂₀ at 25 °C (Δ) and 35 °C (○).

### 3.5 Conclusion

It is known from the literature that the CTABr micellar binding constant of salicylate ion is nearly 100-fold larger in the presence of CTABr micelles compared to that in the presence of C₁₆E₂₀ (Khan & Ismail, 2004). It is now common belief that the viscoelastic behavior of aqueous CTABr micellar solution containing sodium salicylate is caused by the strong CTABr micellar binding of sodium salicylate. However, the perception has never been supported by the quantitative determination of such binding constant. The new
and interesting finding described in this chapter is that CTABr/M₂X/H₂O micellar solution (with $K_{X}^{Br}$ or $R_{X}^{Br} \approx 42$) contains wormlike micelles whereas CTABr/M₂X/C₁₆E₂₀/H₂O micellar solution (with $\mu K_{X}^{Br}$ or $\mu R_{X}^{Br} \approx 16$) contains spherical micelles, with $M₂X = \text{disodium salicylate}$. This presents a quantitative correlation between the magnitude of counterion (X) binding constant with CTABr ($K_{X}^{Br}$ or $R_{X}^{Br}$) and X-induced CTABr micellar growth. It is also important to note that the structural feature, as well as viscosity of CTABr/M₂X/C₁₆E₂₀/H₂O micellar solutions, can be manipulated by just changing the concentration of C₁₆E₂₀.
CHAPTER 4: STUDY OF CATIONIC AND NONIONIC MIXED MICELLES WITH NaBr AND 3,5-Cl₂C₆H₃CO₂Na BY THE USE OF PROBE NUCLEOPHILIC REACTION OF PIPERIDINE WITH IONIZED PHENYL SALICYLATE

4.1 Introduction

There is no dispute on the recent rises and needs for new and consistent scientific information in the field of research on micelles (Stang, 2012). Surface active substances (SAS), popularly called surfactants, form micelles of different characteristics and they have been discovered for the past 10 decades (Menger, 1979). It has also been unanimously believed that changes in cationic micellar behaviors, from one structural feature to another, are related to the counterion (X) affinity to their surfaces (Gravsholt, 1976; Oelschlaeger et al., 2010; Penfold et al., 2004; Rao et al., 1987; Singh et al., 2009; Vermathen et al., 2002) and different investigations on qualitative NMR studies on the cationic micellar affinity of X ions have been reported (Rao et al., 1987; Singh et al., 2009; Vermathen et al., 2002). Some di-substituted benzoate salts were studied based on NMR and the counterions X (including 3,5-Cl₂C₆H₃CO₂⁻) were reported to be inserted into the micellar hydrophobic core/hydrophilic head interface (Kreke et al., 1996). Rheological studies, small angle neutron scattering (SANS), and cryo-TEM images have also revealed the micellar growth and its formation for the X ions (Carver et al., 1996).

There have been quite a number of reports that provided various kinetic models which were used to quantitatively correlate the observed data for the rate of micellar catalysed reactions (Khan, 2006). However, most of the studies were focused on the pure micellar system (Eads & Robosky, 1999) and very few were reported based on mixed micellar

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system (Junquera & Aicart, 2002). Furthermore, theoretical studies on the structure of mixed micelles began a few decades ago (Goldsipe & Blankschtein, 2007) and the detail explanations on their characteristic features are not yet well cleared relative to those of pure micellar systems. There was an attempt, in 1998 (Davies & Foggo, 1998), to explain observations based upon the effects of mixed micelles on the kinetic reaction rate using Multiple Micellar Pseudophase (MMPP) models. But that was carried out to study the mixed anionic-nonionic micellar combination. Another study (Bunton et al., 1993), however, presented the use of Pseudophase (PP) micellar model to explain the rate of reactions affected by mixed cationic-nonionic micellar system. The PP micellar model merged with an empirical equation (Eq. 3.1) (Khan & Ismail, 2003) was used to treat the results obtained in this study.

The behavior of pure cationic micelles (CTABr), for the reaction of piperidine with ionised phenyl salicylate, in the presence of MX, 3,5-dichlorosodium benzoate (3,5-Cl₂C₆H₃CO₂Na), was recently studied (Razak et al., 2014). However, the study has not reported such behavior in the presence of mixed micelles. It has been known for nearly three decades that the counterionic salts affect the physicochemical properties of mixed aqueous ionic-nonionic surfactants (Dar et al., 2010; Karayil et al., 2016; Sidim, 2016). Effects of the concentrations of moderately hydrophobic counterions on the structural features of iomic micelles in mixed aqueous ionic-nonionic surfactants have been reported rarely, although such systems are very important industrially as well as technologically (Dar et al., 2010). The effects of sodium benzoate (NaBz), sodium hexanoate (NaHx) and NaCl on the associated physicochemical properties of polymer-cationic surfactant mixed system have been studied and the qualitative interpretation of the findings is given in detail (Dar et al., 2006; Dar et al., 2010; Jan et al., 2007; Mir et al., 2009). A quantitative interpretation of these results (Dar et al., 2006; Dar et al., 2010; Jan et al., 2007; Karayil et al., 2016; Mir et al., 2009; Sidim, 2016) and related studies
(Lin et al., 2016; Wang et al., 2015; Yan & Zhao, 2015; Zhang et al., 2013) is difficult because of the unavailability of the values of the counterion binding constants with the ionic surfactants in the absence and presence of nonionic surfactant or polymer. In the continuation of the study on the determination of the hydrophilic and moderately hydrophobic counterions binding constants with CTABr in the absence and presence of C_{16}E_{20} (Fagge et al., 2016), the following new findings are reported on: (i) the effects of [C_{16}E_{20}] on the binding affinity of X\(^-\) with CTABr, (ii) the rheological study of mixed aqueous CTABr/MX/C_{16}E_{20}/H\(_2\)O (MX = 3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)Na) solution and (iii) the possible quantitative relationship between the values of ion exchange constants (R\(_{X}^{Br}\) or K\(_{X}^{Br}\)) and the structural features of CTABr/MX/C_{16}E_{20}/H\(_2\)O (MX = 3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)Na).

The choice of MX as 3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)Na was motivated by nearly 4-fold larger mean value of R\(_{X}^{Br}\) or K\(_{X}^{Br}\) for X = 3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)^- than that for X = salicylate ion (Fagge et al., 2016). The results and their plausible explanations are described in this chapter. It is perhaps noteworthy that this constitutes the second report where the effect of mixed micelles, CTABr-C_{16}E_{20}/H\(_2\)O, on the counterion binding constant have been studied quantitatively.

4.2 Methodology

4.2.1 Reagents and chemicals

All the reagents and chemicals mentioned in section 3.2.1, except M\(_2\)X (M\(_2\)X = disodium salicylate, 2-NaOC\(_6\)H\(_4\)CO\(_2\)Na), were the same in this section. Their methods of preparations, as well as concentrations, were also the same. Another salt, MX (3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)Na) brought by Sigma-Aldrich, with 97% purity, was used instead. The standard solutions of 0.2 M MX (3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)Na) were prepared by adding 0.25 M NaOH to 0.2 M solution of 3,5-dichlorobenzoic acid (3,5-Cl\(_2\)C\(_6\)H\(_3\)CO\(_2\)H) which was obtained from Aldrich with 97% purity and it was recrystallized before preparation.
4.2.2 Kinetic method

The details are the same as in section 3.2.2.

4.2.3 Use of semi empirical kinetic, SEK, method to find the values of relative counterion binding constants ($K_X^{Br}$ or $R_X^{Br}$) for $X = 3,5$-$Cl_2C_6H_3CO_2^-$

The details are the same as in section 3.2.3.

4.2.4 Rheological study

The details are the same as in section 3.2.4.

4.3 Results

4.3.1 Effect of [NaBr] on $k_{obs}$ for the piperidinolysis of PhS$^-$ at lower concentrations of C$_{16}$E$_{20}$ in mixed CTABr-C$_{16}$E$_{20}$ and 35 °C

The kinetic experiments on the effects of [NaBr] for the reaction of 0.10 M Pip, 0.20 mM PSH and 0.030 M NaOH in the presence of pure CTABr and mixed CTABr-C$_{16}$E$_{20}$ on $k_{obs}$ (with the NaBr concentration range from 0.00–0.700 M) were conducted at 35 °C and 370 nm. The value of [CTABr]$_T$ is 0.006 M with 0.00 M C$_{16}$E$_{20}$. Similar observations were obtained by increasing [C$_{16}$E$_{20}$] to 0.6 µM and 0.06 mM. The results are presented graphically in Figure 4.1.

4.3.2 Effect of [3,5-$Cl_2C_6H_3CO_2Na$] on $k_{obs}$ for the piperidinolysis of PS$^-$ at a constant concentration of pure CTABr and 35 °C

Other kinetic experiments were also conducted at constant 0.10 M Pip, 0.20 mM PSH and 0.03 M NaOH in the presence of 0.006 M CTABr and various values [3,5-$Cl_2C_6H_3CO_2Na$] (0.00–0.08 M). Similar results were obtained by further increasing the concentration of CTABr to 0.010 and 0.015 M. The values of $k_{obs}$ obtained are shown in Table 4.1.
4.3.3 Effect of [3,5-Cl₂C₆H₃CO₂Na] on $k_{obs}$ for the piperidinolysis of PS⁻ at a constant concentration of C₁₆E₂₀ and 35 °C

Other kinetic experiments for the piperidinolysis of PS⁻ at various [3,5-Cl₂C₆H₃CO₂Na] (within the range of 0.00–0.20 M) and 0.030 M NaOH were carried out. They were performed at [C₁₆E₂₀]$_T$ = 0.001 M, 370 nm and 35 °C. The value of [C₁₆E₂₀]$_T$ was increased to 0.003, 0.006, 0.008, 0.010, and 0.015 M. The kinetic parameters obtained are presented in Appendix E (with [C₁₆E₂₀]$_T$ = 0.001, 0.003 and 0.006 M) and Appendix F (with [C₁₆E₂₀]$_T$ = 0.008, 0.0010 and 0.015 M).

4.3.4 Effect of [3,5-Cl₂C₆H₃CO₂Na] on $k_{obs}$ for the piperidinolysis of PS⁻ at various concentrations of mixed CTABr-C₁₆E₂₀ and 35 °C

Two sets of kinetic experiments were conducted at constant 0.10 M Pip, 0.20 mM PS⁻, 0.03 M NaOH and different [3,5-Cl₂C₆H₃CO₂Na] (0.00–0.04 M) in the presence of lower concentrations of C₁₆E₂₀ of the mixed CTABr-C₁₆E₂₀ micelles ([CTABr]$_T$ = 0.006 M with [C₁₆E₂₀]$_T$ = 6.0 µM).

Similar results were obtained upon increasing [C₁₆E₂₀]$_T$ to 0.06 mM and the observed data are presented in Table 4.2.

Three sets of kinetic experiments were also conducted at constant 0.10 M Pip, 0.20 mM PS⁻, 0.03 M NaOH, and different [3,5-Cl₂C₆H₃CO₂Na] (0.00–0.08 M) in the presence of higher concentrations of C₁₆E₂₀ of the mixed CTABr-C₁₆E₂₀ micelles ([CTABr]$_T$ = 0.006, 0.010 and 0.015 M with 0.006 M C₁₆E₂₀). Similar results were obtained upon increasing [C₁₆E₂₀]$_T$ to 0.010 and 0.015 M and the plots of $k_{obs}$ against [3,5-Cl₂C₆H₃CO₂Na] are presented in Figures 4.2, 4.3 and 4.4, respectively.
4.3.5 Rheological characteristics of aqueous pure CTABr micellar solutions at various [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na], 25 and 35 °C

Aqueous solution mixtures containing constant [Pip], [PS$^-$], and [NaOH] in the presence of 0.015 M CTABr and different [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] were rheologically measured. The experiments were conducted at the steady-shear response and two distinct temperatures (25 and 35 °C). Different values of shear viscosity ($\eta$) at various shear rates ($\gamma^\prime$) were determined. The results are presented, using log-log sketches of $\eta$ vs $\gamma^\prime$, in Figures 4.5 (a) and (b) at, respectively, 25 and 35 °C.

4.3.6 Rheological characteristics of aqueous mixed CTABr-C$_{16}$E$_{20}$ micellar solutions at various [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na], 25 and 35 °C

To study the effects of mixed micelles, another aqueous solution mixtures of constant [Pip], [PS$^-$], [NaOH], and mixed 0.015 M CTABr and 0.006 M C$_{16}$E$_{20}$ at different [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na], were subjected to rheometric measurements. The experimental conditions were similar as that in 4.3.5 above and different values of $\eta$ at different $\gamma^\prime$ were also determined. Different observations were obtained in the presence of 0.006 M C$_{16}$E$_{20}$ and the results are presented, using log–log sketches of $\eta$ vs. $\gamma^\prime$, in Figures 4.6 (a) and (b) at, respectively, 25 and 35 °C.
Figure 4.1: Plots showing the relationship between $m_{\text{kobs}}$ (where superscript “m” represents mixed micelles) and [NaBr] for the reaction of Pip and PS$^{-}$ at three different constant [CTABr]$^T$ + [C$_{16}$E$_{20}$]$^T$ = 0.006 M + 0.00 M (●), 0.006 M + 0.6 μM (♦) and 0.006 M + 0.060 mM (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant ($k_{\text{calcd}}$). Insert: The plots for magnified scale for the data points at lower values of [NaBr].

Figure 4.2: Plots showing the relationship between $m_{\text{kobs}}$ (where superscript “m” represents mixed micelles) and [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] for the reaction of Pip and PS$^{-}$ at three different constant [CTABr]$^T$ + [C$_{16}$E$_{20}$]$^T$/M = 0.006 + 0.006 (●), 0.006 + 0.010 (♦) and 0.006 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant ($k_{\text{calcd}}$). Insert: The plots for magnified scale for the data points at lower values of [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na].
Table 4.1: Pseudo first-order rate constants ($k_{\text{obs}}$) for the reaction of Pip with PS$^-$ at 0.006, 0.010 and 0.015 M CTABr at different [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na].

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<th>[MX]$^b$ M</th>
<th>[CTABr]$^c$ = 0.006 M</th>
<th>0.010 M</th>
<th>0.015 M</th>
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<td>$10^4 k_{\text{calcd}}^e s^{-1}$</td>
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<td>26.6 ± 0.3$^f$</td>
<td>25.4 ± 0.2$^f$</td>
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<td>28.3 ± 0.4</td>
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<td>28.8 ± 0.2</td>
<td>27.3 ± 0.2</td>
<td>26.9 ± 0.2</td>
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<td>0.004</td>
<td>31.8 ± 0.3</td>
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<td>0.006</td>
<td>51.3 ± 0.6</td>
<td>42.4 ± 0.2</td>
<td>33.0 ± 0.3</td>
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<td>0.008</td>
<td>94.4 ± 0.6</td>
<td>75.0 ± 0.6</td>
<td>54.5 ± 0.3</td>
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<td>123.0 ± 1.3</td>
<td>114.5 ± 1.5</td>
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<td>127.8 ± 1.7</td>
<td>99.2 ± 0.7</td>
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<tr>
<td>0.014</td>
<td>163.4 ± 1.4</td>
<td>142.0</td>
<td>110.4 ± 1.2</td>
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<tr>
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<td>176.7 ± 1.6</td>
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<td>0.018</td>
<td>182.8 ± 1.9</td>
<td>149.3 ± 1.9</td>
<td>127.5 ± 1.2</td>
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<td>192.3 ± 2.2</td>
<td>157.5 ± 2.1</td>
<td>137.0 ± 1.2</td>
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<tr>
<td>0.022</td>
<td>198.5 ± 2.2</td>
<td>166.7 ± 1.8</td>
<td>149.6 ± 1.2</td>
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<tr>
<td>0.026</td>
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<td>183.2 ± 2.0</td>
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<tr>
<td>0.030</td>
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<td>196.2 ± 2.0</td>
<td>162.5 ± 1.4</td>
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<td>206.0 ± 2.1</td>
<td>172.1 ± 1.8</td>
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<td>211.7 ± 1.8</td>
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<td>233.1 ± 1.9</td>
<td>209.1 ± 1.6</td>
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$^a$[PSH]$_0$ = 0.2 mM, [Pip] = 0.1 M, [NaOH] = 0.03 M, $\lambda = 370$ nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. $^b$Total concentration of 3,5-Cl$_2$C$_6$H$_3$CO$_2$Na. $^c$Total concentration of CTABr. $^d$Observed pseudo first order rate constant. $^e$Pseudo first order rate constant calculated from Eq. 3.13 with parameters listed in Table 4.4. $^f\theta = F_{X/S}(k_w^2[Pip])$ and $K_{X/S} = K_{X/S}(1 + K_0^0(CTABr))$. $^g$Error limits are standard deviations.
Table 4.2: Pseudo-first-order rate constants ($m_{\text{kobs}}$) for the reaction of piperidine with anionic phenyl salicylate (PS$^-$) at 0.006 M CTABr in the presence of 0.600 μM, and 0.060 mM C$_{16}$E$_{20}$ and different [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na].

<table>
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<th>[MX]$^b$</th>
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<td>M</td>
<td>10$^4 m_{\text{kobs}}$ s$^{-1}$</td>
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Footnote $a, b, $ and $c$ are the same as in Table 4.1. $d$Total concentration of C$_{16}$E$_{20}$. $e$Observed pseudo first order rate constant. $f$Pseudo first order rate constant calculated from Eq. 3.13. $g$Error limits are standard deviation.
Figure 4.3: Plots showing the relationship between $^{m}\text{k}_{\text{obs}}$ (where superscript “m” represents mixed micelles) and [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] for the reaction of Pip and PS$^-$ at three different constant [CTABr]$_T$ + [C$_{16}$E$_{20}$]$_T$/M = 0.010 + 0.006 (●), 0.010 + 0.010 (♦) and 0.010 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant (k$_{\text{calcd}}$). Insert: The plots for magnified scale for the data points at lower values of [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na].

Figure 4.4: Plots showing the relationship between $^{m}\text{k}_{\text{obs}}$ (where superscript “m” represents mixed micelles) and [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] for the reaction of Pip and PS$^-$ at of three different constant [CTABr]$_T$ + [C$_{16}$E$_{20}$]$_T$/M = 0.015 + 0.006 (●), 0.015 + 0.010 (♦) and 0.015 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant (k$_{\text{calcd}}$). Insert: The plots for magnified scale for the data points at lower values of [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na].
Figure 4.5: Plots representing shear viscosity ($\eta$) against shear rate ($\dot{\gamma}$) for the piperidinolysis of PS$^-$ containing 0.015 M CTABr and [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na]/M = (a) 0.004 (•) 0.007 (□) 0.015 (▲) 0.025 (♦) 0.040 (○) and 0.070 (◊) at 25 °C and (b) 0.004 (•) 0.007 (□) 0.015 (▲) 0.025 (♦) 0.040 (○) and 0.070 (◊) at 35 °C.
Figure 4.6: Plots representing shear viscosity (η) against shear rate (γ̇) for the piperidinolysis of PS− containing 0.015 M CTABr, 0.006 M C₁₆E₂₀ and [3,5-Cl₂C₆H₃CO₂Na]/M = (a) 0.004 (•) 0.007 (□) 0.015 (▲) 0.025 (●) 0.040 (○) and 0.070 (◊) at 25 °C and (b) 0.004 (•) 0.007 (□) 0.015 (▲) 0.025 (●) 0.040 (○) and 0.070 (◊) at 35 °C.
4.4 Discussion

4.4.1 Explanation of kinetic observations for the piperidinolysis of PS\textsuperscript{−} in the presence of pure C\textsubscript{16}E\textsubscript{20} micelles at various [MX] and 35 °C

The results obtained showed similar effect as explained in section 3.4.1 and the values of kinetic parameters are presented in Table 4.3.

Table 4.3: Values of kinetic parameters for the reaction of Pip and PS\textsuperscript{−} in the presence of 3,5-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CO\textsubscript{2}Na at different [C\textsubscript{16}E\textsubscript{20}]\textsubscript{T} and 35 °C.\textsuperscript{a}

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<th>[C\textsubscript{16}E\textsubscript{20}]\textsubscript{T} \textsuperscript{b} M</th>
<th>k\textsubscript{obs}\textsuperscript{0} \textsuperscript{c} s\textsuperscript{−1}</th>
<th>k\textsubscript{obs}\textsuperscript{MX (max)} \textsuperscript{d} s\textsuperscript{−1}</th>
<th>%NSE\textsuperscript{e}</th>
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</tr>
</tbody>
</table>

\textsuperscript{a}[PSH]\textsubscript{0} = 0.20 mM, [NaOH] = 0.03 M, [Pip] = 0.10 M, λ = 370 nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. \textsuperscript{b}Total concentration of C\textsubscript{16}E\textsubscript{20}. \textsuperscript{c}k\textsubscript{obs}\textsuperscript{0} = k\textsubscript{obs} at [MX] = 0 (or average value of similar values of k\textsubscript{obs} at various [MX]). \textsuperscript{d}k\textsubscript{obs}\textsuperscript{MX (max)} = k\textsubscript{obs} at the maximum value of [MX]. \textsuperscript{e}Percent negative salt effect, %NSE calculated from Eq. 3.12

4.4.2 Explanation of kinetic results at constant concentration of pure CTABr micelles, various values of [3,5-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CO\textsubscript{2}Na] and 35 °C

The values of k\textsubscript{obs} for the reaction of 0.10 M Pip and 0.20 mM PSH in basic medium with [CTABr]\textsubscript{T} = 0.006, 0.010 or 0.015 M, [C\textsubscript{16}E\textsubscript{20}]\textsubscript{T} = 0, and different concentration of 3,5-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CO\textsubscript{2}Na (Table 4.1) obey semi empirical Eq. 3.13. The values of θ and K\textsubscript{X/S}, obtained at different [CTABr]\textsubscript{T}, were calculated using, respectively, Eqs. 3.13 and 3.15, and are presented in Table 4.4.
4.4.3 Ion exchange catalysis

Perhaps it is noteworthy that the observed data described in Tables 4.1 and 4.2, and the plots of Figures 4.1–4.4 where the increase in $k_{\text{obs}}$ with increasing [MX] represents catalytic effects of MX. The study carried out to discover the effects of MX (= sodium 4-chlorobenzoate) on $k_{\text{obs}}$ for piperidinolysis of PS$^-$ revealed the decrease of nearly 10% with the increase in [MX] from 0.0 to $\leq 0.2$ M at constant [C$_{16}$E$_{20}$] within its range 5–15 mM and [CTABr]$r = 0$ (Fagge & Khan, 2016). Thus, the observed results exhibited by Tables 4.1, 4.2 and Figures 4.1–4.4 cannot be attributed to ionic strength/salt effect. Similar observations have been presented in several reports on related studies where the nonlinear increase in $k_{\text{obs}}$ with an increase in [MX] at a constant [cationic micelles] is ascribed to the occurrence of ion exchange process X$^-$/PS$^-$ at the cationic micellar surface (Khalid et al., 2016; Khan, 2006; Khan, 2010). This characteristic behavior of CTABr/MX/H$_2$O/C$_{16}$E$_{20}$ catalysis is referred to ion exchange catalysis, where the origin of catalysis of MX is the ion exchange X$^-$/PS$^-$. It is evident from Eq. 3.13 that $0K^{X/S}$ represents apparent catalytic constant ($^{X}k_{\text{cat}}$) of MX. Thus, the replacement of $0K^{X/S}$ in Eq. 3.13 gives Eq. 4.1.

$$k_{\text{obs}} = \frac{k_0 + ^Xk_{\text{cat}} ([MX] - [MX]_{0}^{\text{op}})}{1 + K^{X/S} ([MX] - [MX]_{0}^{\text{op}})}$$

where $k_0 = k_{\text{obs}}$ at [MX] = [MX]$_{0}^{\text{op}}$, and [MX]$_{0}^{\text{op}}$ represents the optimum values of [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] at which further increase in [MX] or [M$_2$X] is believed to have no effect on ion exchange X$^-$/HO$^-$ and X$^-$/Br$^-$ occurring in the CTABr micellar phase (Khan, 2010) and were obtained by the use of iterative method explained in detail in the literature (Khan & Ismail, 2003; Khan & Ismail, 2009). The values of $K^{X/S}$ and $^{X}k_{\text{cat}}$ were determined by the use of nonlinear least squares method. The values of $k_0$ were found experimentally by
carrying out kinetic runs at constant [CTABr]τ and [MX] = 0 (Table 4.4). The optimum values of [3,5-Cl2C6H3CO2Na] ([MX]0) at various [CTABr]τ were determined as described in the past (Khan & Ismail, 2003) and are presented in Table 4.4.

It has been described in detail elsewhere (Khan, 2010) that a plausible reaction mechanism in terms of psuedophase micellar model and empirical equation (Eq. 3.13) can lead to Eq. 4.1 with \( K_{X/S} \) and \( x_k_{cat} \) represented by Eqs 3.15 and 4.2, respectively. It has been noticed from Eq. 3.15 that increase in [CTABr]τ results in the corresponding decrease in the values of \( K_{X/S} \) (so long as \( K_{X/S} \) does not depend on [CTABr]τ). This observation agrees with the results in Table 4.4 where \( K_{X/S} = 128, 82 \) and 57 M\(^{-1}\) at respectively [CTABr]τ = 0.006, 0.010 and 0.015 M. But the values of \( K_{X/S} \) (Table 4.4) were determined using Eq. 3.15.

\[
x_k_{cat} = F_{X/S}(k_W^2[Pip]_τ)K_{X/S}
\] (4.2)

where \( F_{X/S} \) is an empirical constant and its appearance in Eq. 4.2 is described in detail elsewhere (Khan, 2010), \( k_W^2 \) represents second-order rate constant for the nucleophilic reaction of Pip with ionized PSH (PS\(^-\)).

Perhaps, it is noteworthy that the calculated values of \( K_{X/S} \) and \( k_{calcd} \) were turned out to be exactly the same at a particular value of [CTABr]τ which is evident from Tables 4.1 and 4.2, and the plots of Figures 4.1–4.4 where the solid lines are drawn through the calculated values of the rate constant, \( k_{calcd} \).

To determine the values of conventional ion exchange constant/relative counterion binding constant \( (K_{X}^{Br}) \), the normalised values of both \( K_{X/S} \) (\( K_{X/S}^{n} = F_{X/S}K_{X/S} \)) and \( K_{Br/S} \) \((K_{Br/S}^{n} = F_{Br/S}K_{Br/S} \)) (as discussed in section in section 3.4.2) are required. The values of \( K_{X/S}^{n} \) are presented in Table 4.4. The values of \( K_{X}^{Br} \) were calculated from Eq. 3.16 and the
calculated values of $K_{X/S}^n$ and the reported value of $K_{Br/S}^n$ ($= 25 \text{ M}^{-1}$) (Khan, 1997a; Khan et al., 2000; Khan & Ismail, 2007). Similarly, the values of $R_{X}^{Br}$ were calculated from Eq. 3.17 and the calculated values of $(\alpha K_{X/S})^{np}$ and $(\alpha K_{Br/S})^{sp}$ in Table 4.4. These calculated values of $K_{X}^{Br}$ or $R_{X}^{Br}$ are summarised in Table 4.4.

Apparent experimental proof reported that there exist a consistently respective increase and decrease in hydrophobicity and hydrophilicity of micellar phase when the separation between the interior and exterior regions of the micelles is increased (Laschewsky, 2003). The counterion $X$ (3,5-Cl$_2$C$_6$H$_3$CO$_2^{-}$) has chloro substituents (Cl) and a carboxylate ion (COO$^{-}$) which are, respectively, hydrophobic and hydrophilic in nature. The two chloro substituents, at position 3 and 5 of $X$, are assumed to be in a micellar region of almost similar hydrophilic and hydrophobic character. Thus, considering the reported value of $K_{X}^{Br}$ or $R_{X}^{Br}$ ($= 50$) for 3-ClC$_6$H$_4$CO$_2^{-}$ (Razak et al., 2014), the value of $K_{X}^{Br}$ for 3,5-Cl$_2$C$_6$H$_3$CO$_2^{-}$ supposed to have been around 100 if, and only if, the free energy factor (at the expense of groups located at the aromatic segment) would be significant. However, the mean value of $K_{X}^{Br}$ or $R_{X}^{Br}$, (Table 4.4) for 3,5-Cl$_2$C$_6$H$_3$CO$_2^{-}$ is 198. This prediction of $K_{X}^{Br}$ or $R_{X}^{Br}$ value, based upon the number of substituents and their locations in an aromatic region, has a probably failed assumption which depends only on structural behaviours of CTABr/MX. It has not taken into account the changes in shapes and sizes of MX/CTABr with the decrease or increase in values of $K_{X}^{Br}$ or $R_{X}^{Br}$ (Razak et al., 2014). The published results show the existence of mixed vesicle-wormlike micelles at 0.006–0.015 M range of CTABr and various values of [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] (Razak & Khan, 2013).

4.4.4 Explanation of kinetic data at constant mixed CTABr-C$_{16}$E$_{20}$ micelles, various [3,5-Cl$_2$C$_6$H$_3$CO$_2$Na] and 35 °C

The mixed cationic-nonionic (CTABr-C$_{16}$E$_{20}$) micellar system is different from the pure micellar system. To differentiate between the parameters obtained in the mixed
CTABr-C_{16}E_{20} micellar systems and those in the pure ones, a letter “m” is used as a superscript to represent those obtained in the presence of mixed CTABr-C_{16}E_{20} micelles as elaborated in section 3.4.2. It has been explained in section 4.4.2 (the case of pure CTABr micelles) that the values of k_o were determined at constant [CTABr]_T and [3,5-Cl_2C_6H_3CO_2Na] = 0. However, in the case of mixed CTABr-C_{16}E_{20}, the condition has been changed by adding constant concentrations of C_{16}E_{20} (6.0 \times 10^{-7}, 6.0 \times 10^{-5}, 6.0 \times 10^{-3}, 1.0 \times 10^{-2} and 1.5 \times 10^{-2} M) and the corresponding values of m_k are presented in Table 4.5. The values of m_k were also found to fit Eq. 3.13. The values of m[MX]_0^o (Table 4.5) were found to increase with the increase in [CTABr]_T and almost independent of [C_{16}E_{20}]_T. However, these values are comparatively higher than those obtained in the presence of pure CTABr (Table 4.4).

The relationship between m_0 and m_F_X/S is: m_F_X/S = m_0/m_kW, with m_kW = m_k at various [C_{16}E_{20}]_T and [CTABr]_T = [MX] = 0 (m_kW = m_k^2Pip)_T. The values of m_kW are 303.5 \times 10^{-4}, 273.0 \times 10^{-4}, 240.0 \times 10^{-4}, 193.2 \times 10^{-4} and 184.2 \times 10^{-4} s^{-1} at, respectively, 6.0 \times 10^{-7}, 6.0 \times 10^{-5}, 6.0 \times 10^{-3}, 1.0 \times 10^{-2} and 1.5 \times 10^{-2} M constant [C_{16}E_{20}]_T. The values of m_F_X/S (Table 4.5) are independent of the concentration of the mixed CTABr-C_{16}E_{20} micelles. But these values of m_F_X/S were found to be higher than F_X/S in the presence of pure micelles (Table 4.4). The values of m_0 and m_K_X/S, summarised in Table 4.5, were also found to be independent of the concentration of the mixed CTABr-C_{16}E_{20} micelles and were also calculated using Eqs. 3.13 and 3.14. As explained in section 3.4.2, the values of m_K_X/S could not be calculated due to the fact that the values of m_K_S^0 for mixed CTABr-C_{16}E_{20} surfactants are not available for the present study. Hence, Eq. 3.20 should be used for the calculation of m_K_X^{Br}. In addition, the values of m_R_X^{Br} were calculated using Eq. 3.21 and are presented in Table 4.5.
It is evident that in an aqueous solution containing mixed cationic-nonionic surfactants (e.g. CTABr-C₁₆E₂₀), the relatively large hydrophilic headgroup of C₁₆E₂₀ shields the small sized hydrophobic micellar parts of CTABr (Gao et al., 2002).

4.4.5 Explanation of rheometric data in the presence of pure CTABr and mixed CTABr-C₁₆E₂₀ micelles at various [3,5-Cl₂C₆H₃CO₂Na]

Rheological data reveal that different flow curves show various micellar structural behaviours. For pure CTABr (0.015 M), at ≥ 0.004 to ≤ 0.007 M [3,5-Cl₂C₆H₃CO₂Na], there exist flow curves with mild shear thickening behavior at a reasonably high shear rate and at both 25 and 35 °C (Figure 4.5 (a) and (b)) which show unique characteristics of spherical micelles.
Table 4.4: Values of empirical constants, θ, and $K_X/S$ obtained using Eqs. 3.13 and 3.14 with the $[MX]_0^{op}$ values for $MX = 3,5$-Cl$_2$C$_6$H$_3$CO$_2$Na at different $[CTABr]_T$.\(^a\)

<table>
<thead>
<tr>
<th>[CTABr]$_T$ M</th>
<th>$10^4 k_0^e$ s$^{-1}$</th>
<th>$[MX]_0^{op}$ M</th>
<th>$10^3 \theta^{d,1}$ s$^{-1}$</th>
<th>$10^8 k_{cat}^{e}$ M$^{-1}$s$^{-1}$</th>
<th>$F_{X/S}$</th>
<th>$K_{X/S}$ M$^{-1}$</th>
<th>$K_{X/S}^n$ M$^{-1}$</th>
<th>$K_X^B$ or $R_X^B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006$^b$</td>
<td>28.7 ± 0.2$^f$</td>
<td>0.00531</td>
<td>28.1 ± 0.2$^f$</td>
<td>128.0 ± 3.1$^f$</td>
<td>32.6 ± 0.7</td>
<td>0.90$^e$</td>
<td>5504$^b$</td>
<td>4954.0$^e$</td>
</tr>
<tr>
<td>0.010</td>
<td>26.6 ± 0.3</td>
<td>0.00515</td>
<td>27.2 ± 0.4</td>
<td>81.7 ± 3.5</td>
<td>22.2 ± 0.7</td>
<td>0.87</td>
<td>5727</td>
<td>4982.7</td>
</tr>
<tr>
<td>0.015</td>
<td>25.4 ± 0.2</td>
<td>0.00552</td>
<td>25.6 ± 0.3</td>
<td>56.7 ± 1.8</td>
<td>14.5 ± 0.3</td>
<td>0.82</td>
<td>6010</td>
<td>4928.2</td>
</tr>
</tbody>
</table>

Footnote $a$ is the same as in Table 4.1. $^b$Total concentration of CTABr. $^c k_0 = k_{obs}$ at $[MX] = [MX]_0^{op}$. $^d$The values of $\theta$ and $K_X/S$ were calculated from Eqs. 3.13 and 3.14. $^e$The values of $k_{cat}$ and $K_X/S$ were calculated from Eq. 4.1 with the replacement of $0k_X/S$ in Eq. 3.13 by $k_{cat}$. $^f$Limits of error signifies standard deviations. $^g F_{X/S} = \theta/(k_W^2 [Pip]_T)$, where $k_W^2 = k_{obs}$ at $[CTABr]_T = [C_{16}E_{20}]_T$ = 0 and $[Pip]_T = 0.10$ M and the value of $k_W$, under such conditions is 0.322 M$^{-1}$s$^{-1}$. $^h K_{X/S} = K_X^{CBr}(1+K_{S}^{CBr}[CTABr]_T)$, where $K_S^{CBr} = 7 \times 10^3$ M$^{-1}$. $^i K_{X/S}^n = F_{X/S} K_{X/S}$. $^j K_X^B$ or $R_X^B = K_X^{CBr}/ K_{Br/S}$, where $K_{Br/S} = 25$ M$^{-1}$ (Yusof & Khan, 2010).
Table 4.5: Values of empirical constants, $m_0$, and $mK^{X/S}$ obtained using Eqs. 3.13 and 3.14 with the $[MX]_0^{op}$ values for MX = 3,5-Cl$_2$C$_6$H$_3$CO$_2$Na at different concentrations of mixed CTABr-C$_{16}$E$_{20}$.

<table>
<thead>
<tr>
<th>[CTABr]</th>
<th>$[C_{16}E_{20}]^{c/M}$</th>
<th>$10^4 m_k^d s^{-1}$</th>
<th>$10^3 m_{[MX]}_0^{op} M$</th>
<th>$10^3 m_0^e s^{-1}$</th>
<th>$mK^{X/S}/M^{-1}$</th>
<th>$10 mK_{cat}/M^{-1}s^{-1}$</th>
<th>$mF/X/S$</th>
<th>$mK^{X/S}M^{-1}$</th>
<th>$mK_{Br/SH}$</th>
<th>$mK_X^{Br}$ or $mR_X^{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>0.00000006</td>
<td>20.3 ± 0.3$^e$</td>
<td>0.00311</td>
<td>22.7 ± 0.1$^e$</td>
<td>178.2 ± 2.0$^e$</td>
<td>40.4 ± 0.3$^e$</td>
<td>0.8$^b$</td>
<td>142.6$^i$</td>
<td>1.4</td>
<td>102$^k$</td>
</tr>
<tr>
<td>0.006</td>
<td>0.00006</td>
<td>21.1 ± 0.4$^d$</td>
<td>0.00318</td>
<td>20.5 ± 0.1$^d$</td>
<td>192.6 ± 2.5</td>
<td>39.5 ± 0.4</td>
<td>0.8$^b$</td>
<td>154.1</td>
<td>1.8</td>
<td>85.1</td>
</tr>
<tr>
<td>0.006</td>
<td>0.006</td>
<td>33.4 ± 0.4$^d$</td>
<td>0.00352</td>
<td>27.2 ± 0.3$^d$</td>
<td>120.8 ± 4.2</td>
<td>32.9 ± 0.9</td>
<td>1.1$^b$</td>
<td>132.9</td>
<td>1.4$^i$</td>
<td>81.5</td>
</tr>
<tr>
<td>0.006</td>
<td>0.010</td>
<td>34.5 ± 0.4$^d$</td>
<td>0.00317</td>
<td>25.4 ± 0.2$^d$</td>
<td>117.6 ± 3.5</td>
<td>29.8 ± 0.7</td>
<td>1.3$^b$</td>
<td>152.9</td>
<td>2.2$^i$</td>
<td>60.0</td>
</tr>
<tr>
<td>0.006</td>
<td>0.015</td>
<td>35.7 ± 0.4$^d$</td>
<td>0.00318</td>
<td>23.3 ± 0.2$^d$</td>
<td>122.2 ± 3.3</td>
<td>28.5 ± 0.6</td>
<td>1.3$^b$</td>
<td>158.9</td>
<td>1.8$^i$</td>
<td>73.9</td>
</tr>
<tr>
<td>0.010</td>
<td>0.006</td>
<td>30.9 ± 0.3$^d$</td>
<td>0.00534</td>
<td>26.2 ± 0.2$^d$</td>
<td>67.2 ± 1.7</td>
<td>17.6 ± 0.3</td>
<td>1.1$^b$</td>
<td>73.9</td>
<td>1.0$^i$</td>
<td>85.9</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>43.4 ± 0.4$^d$</td>
<td>0.00989</td>
<td>21.2 ± 0.2$^d$</td>
<td>54.3 ± 1.9</td>
<td>11.5 ± 0.3</td>
<td>1.1$^b$</td>
<td>59.7</td>
<td>1.1$^i$</td>
<td>61.1</td>
</tr>
<tr>
<td>0.010</td>
<td>0.015</td>
<td>33.8 ± 0.2$^d$</td>
<td>0.00547</td>
<td>22.5 ± 0.3$^d$</td>
<td>75.4 ± 3.0</td>
<td>17.0 ± 0.5</td>
<td>1.2$^b$</td>
<td>89.5</td>
<td>0.9$^i$</td>
<td>105.3</td>
</tr>
<tr>
<td>0.015</td>
<td>0.006</td>
<td>28.3 ± 0.2$^d$</td>
<td>0.00866</td>
<td>25.7 ± 0.2$^d$</td>
<td>32.2 ± 0.5</td>
<td>8.3 ± 0.1</td>
<td>1.1$^b$</td>
<td>35.4</td>
<td>0.8$^i$</td>
<td>46.6</td>
</tr>
<tr>
<td>0.015</td>
<td>0.010</td>
<td>39.8 ± 0.5$^d$</td>
<td>0.01185</td>
<td>17.2 ± 0.1$^d$</td>
<td>59.4 ± 1.4</td>
<td>10.2 ± 0.2</td>
<td>0.9$^b$</td>
<td>52.9</td>
<td>0.6$^i$</td>
<td>85.3</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
<td>28.5 ± 0.3$^d$</td>
<td>0.00964</td>
<td>22.3 ± 0.2$^d$</td>
<td>48.4 ± 1.3</td>
<td>10.7 ± 0.2</td>
<td>1.2$^b$</td>
<td>58.1</td>
<td>0.8$^i$</td>
<td>73.5</td>
</tr>
</tbody>
</table>

Footnote $a$ is the same as in Table 4.1. $^b$Total concentration of CTABr, $^c$Total concentration of C$_{16}$E$_{20}$, $^d m_k = m_{obs}$ at [MX] = [MX]$_0^{op}$. $^e$The values of $m_0$ and $mK^{X/S}$ were calculated from Eqs. 3.13 and 3.14. $^f$The values of $mK_{cat}$ and $mK^{X/S}$ were calculated from Eq. 4.1 with the replacement of $m_0 mK^{X/S}$ in Eq. 3.13 by $mK_{cat}$. $^g$Limits of error signifies standard deviations. $^h F/X/S = m_0 mK^{X/S}$; with $m_{obs}^{W} = m_{obs}^{W} = m_{obs}^{W} [Pip]_T = 303.5 \times 10^{-4}, 273.0 \times 10^{-4}, 240 \times 10^{-4}, 193.2 \times 10^{-4}$ and $184.2 \times 10^{-4} s^{-1}$ at constant [C$_{16}$E$_{20}]_T (6 \times 10^{-5}, 6 \times 10^{-5}, 0.006, 0.010$ and $0.015 M [C_{16}E_{20}]$ respectively) and [MX] = [CTABr] = $0$. $^i mK^{X/S} = mF/X/S mK^{X/S}$. $^j mK_{Br/SH} = mF_{Br/S} mK_{Br/SH}$ for MX = NaBr. $^k$Data are obtained from reference (Fagge et al., 2016). $^l K_{X}^{Br} = mK^{X/S} mK^{Br/S}$. 


Some flow curves, at $\geq 0.015$ to $\leq 0.025$ M $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, experience shear thinning which indicates a non-Newtonian fluid system. This characteristic shows the possible existence of wormlike micelles (Lu et al., 2008) in the solution. However, at $\geq 0.040$ to $\leq 0.070$ M $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, the system turned back to the shear thickening behavior with relatively higher viscosity values (Figure 4.5 (a) and (b)) (Qiao et al., 2011). The presence of 0.006 M $\text{C}_{16}\text{E}_{20}$ in the mixed CTABr-$\text{C}_{16}\text{E}_{20}$ micelles gives different results at the same $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$.

All the 12 flow curves in Figure 4.6 (a) and (b) give mild shear thickening behavior at a reasonably high shear rate under the entire experimental conditions. It has been concluded that very dilute solution with a very low shear viscosity at a very high shear rate exhibits what is called “Taylor effect” and these could be caused by the presence of $\text{C}_{16}\text{E}_{20}$ as a nonionic surfactant. These observations apparently revealed the presence of only spherical micelles under such experimental conditions.

The plot in Figure 4.7 (representing $\eta_0$ against $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) reveals the existence of two well-defined maxima in the absence of $\text{C}_{16}\text{E}_{20}$ at constant shear rate, 0.015 M CTABr and both 25 (□) and 35 °C (◊). These maxima appeared at specific values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, $([3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{sp})$; (i) 0.015 M ($\eta_0 = 31.2$ mPas) and 0.040 M ($\eta_0 = 9.3$ mPas) at 25 °C and (ii) 0.015 M ($\eta_0 = 13.5$ mPas) and 0.040 M ($\eta_0 = 4.8$ mPas) at 35 °C. It is clearly evident, therefore, that at both temperatures, the two maxima occurred at the same values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{sp}$. But the increase in the temperature (from 25 to 35 °C) decreased the values of $\eta_0$ from 31.2 to 13.9 mPas and 9.3 to 4.8 mPas, at respectively, 0.015 and 0.040 M values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{sp}$. 
Despite the fact that reports on the occurrence of maxima in the graph of shear viscosity against [MX] (for a solution of cationic surfactants) are almost common (Davies et al., 2006; Dreiss, 2007; Lin et al., 2009), the detailed explanation of the reaction for the source of those maxima has not yet been apprehended at the molecular level (Davies et al., 2006; Ziserman et al., 2009). Nonetheless, it has been accepted from previous reports (Abdel-Rahem, 2008; Davies et al., 2006) that the appearance of these maxima (under such experimental conditions) is a sign of the presence of wormlike/twisted wormlike micelles in a solution. Contrarily, there was no existence of maxima (Figure 4.7) in the presence of mixed CTABr-C_{16}E_{20} ([CTABr]_T = 0.015 M and [C_{16}E_{20}]_T = 0.006 M) at constant shear rate and both 25 (Δ) and 35 °C (○). But the values of η_o, not different from that of water, have also decreased due to the temperature variation from 25 to 35 °C.

Although specific ion effects on structural features of aqueous ionic surfactant aggregates have been known for the last nearly more than two decades and thousands of papers have been published, the basic forces responsible for such specific effect remain unclear both theoretically and experimentally (Romsted, 2007).

It is considered to be useful to develop reversible micelle-vesicle conversions by changing a physical parameter such as pH, temperature or pressure of the medium. Such approach might provide an understanding of fundamental principles of aqueous surfactants structural transitions from micelles to vesicles (Maeda et al., 2006). The study described in this chapter reveals that the presence of 6 mM C_{16}E_{20} has caused almost complete transformation of mixed vesicles and wormlike micelles to mere spherical micelles.
Figure 4.7: Plots representing zero shear viscosity ($\eta_0$) at constant shear rate ($\dot{\gamma}$) against $[3,5$-$C_6H_3CO_2Na]$ with 0.015 M CTABr in the absence of $C_{16}E_{20}$ at 25 °C (□) and 35 °C (◊), and the presence of 0.006 M $C_{16}E_{20}$ at 25 °C (Δ) and 35 °C (○).

Similarly, the presence of 6 mM $C_{16}E_{20}$ reduced the values of $R_X^{Br}$ or $K_X^{Br}$ from 198 to 81. This is considered to be a quantitative correlation between the values of $R_X^{Br}$ or $K_X^{Br}$ and $X$-induced CTABr micellar growth. It is interesting to note that the similar effect of $C_{16}E_{20}$ could be observed ($R_X^{Br}$ or $K_X^{Br} = 102$) at its concentration of 0.06 mM (Table 4.3).

4.5 Conclusion

Perhaps the most notable finding in this chapter is the reduction of the value of $K_X^{Br}$ or $R_X^{Br}$ from 198 to 78 due to presence of 0.06 mM $C_{16}E_{20}$ in the mixed aqueous solution containing 15 mM CTABr and different values of $[NaX]$ with $X = 3,5$-$C_6H_3CO_2^-$. The values of $mK_X^{Br}$ or $mR_X^{Br}$ remain independent of $[C_{16}E_{20}]$ within the range of 0.06–15 mM. Varying the concentration of $C_{16}E_{20}$ could be a method to achieving changes in the structural as well as the viscoelastic behaviour of aqueous CTABr/$C_{16}E_{20}$/MX (MX = inert organic salt). It can be concluded that the nearly 2½-fold lower values of $mR_X^{Br}$ or
$mK_X^{Br}$ for the aqueous mixed CTABr/C$_{16}$E$_{20}$/3,5-Cl$_2$C$_6$H$_3$CO$_2$Na micellar solution is related to the addition of a nonionic surfactant, C$_{16}$E$_{20}$. This quantitative correlation allows the prediction of structural behaviours of aqueous solutions of both pure CTABr and mixed CTABr-C$_{16}$E$_{20}$ surfactant at different [MX] on the basis of experimentally determined $R_X^{Br}$ or $K_X^{Br}$ values.
CHAPTER 5: KINETICS AND MECHANISM OF COUNTERIONIC SALT (4-
CIC6H4CO2Na)-CATALYZED PIPERIDINOLYSIS OF ANIONIC PHENYL
SALICYLATE IN THE PRESENCE OF CATIONIC-NONIONIC MIXED
MICELLES

5.1 Introduction

Micelles (surfactant aggregates) have been drawing many attentions in nanoscience and nanotechnology fields of research for more than a century (Menger, 1979). Their numerous applications have been practiced, for instance, in district heating and cooling (DHC) systems as drag reducers (Ezrahi et al., 2006; Yang, 2002) and petroleum industries (Walker, 2001). The structural growths in ionic micelles were believed to be dependent upon the strength of the counterion, X, binding to the cationic micelles (Oelschlaeger et al., 2010; Rao et al., 1987; Singh et al., 2009). Kunz and his co-authors attempted to provide a qualitative correlation of X-induced micellar growth based upon the cationic micellar hydrophilic head and X interactions of Hofmeister anions (Kunz et al., 2004). However, the limitations on the quantitative measurements of these bound counterions are yet to be solved (Geng et al., 2006) especially when it comes to mixed surfactants systems. Perhaps it is worth to ask about the outcome of pure cationic micellar structure (example spherical, wormlike or vesicle) if nonionic surfactant (such as polyethylene glycol hexadecyl ether, C16E20) is added to the solution.

Several studies were published on the role of different inert salts in modifying the structural features of cationic micelles in aqueous solutions and, directly or indirectly, believed that these salts influence the micellar structural growth (Gravsholt, 1976; Harada et al., 1988; Zhang et al., 2007). In addition, some studies (Razak & Khan, 2013; Razak

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3This chapter has been accepted for publication by Progress in Reaction Kinetics and Mechanism; ISI indexed Journal
et al., 2016; Yusof et al., 2013) reported the possible quantitative correlations between the CTABr micellar binding constants and the counterion and/or temperature-induced micellar structural growth. These studies (Razak & Khan, 2013; Razak et al., 2016; Yusof et al., 2013) and some related ones (Khan, 1997b, 2010; Lajis & Khan, 1998) used semi empirical kinetic, SEK, method to determine the values of relative counterion binding constant, $K_{X}^{Br}$ or $R_{X}^{Br}$ (with $R_{X}^{Br} = K_{X}/K_{Br}$ where the values of CTABr micellar binding constants, $K_{Br}$ and $K_{X}$, were derived from kinetic parameters obtained in the presence of micelles with different structural features) (Khan & Sinasamy, 2011). However, these reports lack information on the reliable mechanism(s) of the effects of nonionic surfactants in cationic micellar structural transition which opens up a possibility of optimising the use of mixed micelles in advanced technologies and industries nowadays (Yusof & Khan, 2013).

Khan reported (Khan, 2006) some studies where the data obtained for the cationic micellar mediated reactions were quantitatively correlated using several models. Davies and Foggo have also made a significant attempt to explain their findings (Davies & Foggo, 1998) on a mixed anionic-nonionic micellar system using Multiple Micellar Pseudo Phase (MMPP) models. In another report, Bunton and his co-authors have used the Pseudophase (PP) micellar model (Bunton et al., 1993) to demonstrate on the reactions involving mixed cationic-nonionic micellar systems. This PP micellar model has been coupled with an empirical equation (Eq. 3.1) (Khan & Ismail, 2003) to treat the results of the present study.

We report, in this chapter; (i) the use of SEK method (described in detail elsewhere (Yusof & Khan, 2013)) and (ii) the rheometric observations, to correlate the relative counterion binding constants for CTABr/MX/H$_2$O solution (MX = 4-ClC$_6$H$_4$CO$_2$Na) systems and counterion-induced CTABr micellar structural growth in the presence of
C_{16}E_{20} (CTABr/C_{16}E_{20}/MX/H_{2}O). The effort in providing some highlights on how the presence of nonionic surfactant, C_{16}E_{20}, influences the decrease in the mean values of relative counterion binding constant ($k^{Br}_{X}$ or $R^{Br}_{X}$), as well as micellar structural growth, were also made. The observed results and their probable explanations are described in subsequent section.

5.2 Methodology

5.2.1 Reagents

All the reagents and chemicals used in section 3.2.1, except M_{2}X, were the same in this section. Their methods of preparations, as well as concentrations, were also the same. Another salt, MX = 4-ClC_{6}H_{4}CO_{2}Na, brought by Sigma-Aldrich with 99% purity, was used instead. The standard solutions of 0.2 M MX (4-ClC_{6}H_{4}CO_{2}Na) were prepared by adding 0.25 M NaOH to 0.2 M solution of 4-ClC_{6}H_{4}CO_{2}H which was obtained from Sigma-Aldrich with 99% purity.

5.2.2 Kinetic and rheometric studies

The details of the kinetics and the rheometric studies are the same as in section 3.2.2 and 3.2.4 respectively.

5.2.3 Use of semi empirical kinetic, SEK, method for the determination of $K^{Br}_{X}$ or $R^{Br}_{X}$ for X = 4-ClC_{6}H_{4}CO_{2}^{-}

The details are the same as in section 3.2.3.

5.3 Results

5.3.1 Effect of [4-ClC_{6}H_{4}CO_{2}Na] on $k_{obs}$ for the reaction of Pip with PS^{-} at constant concentration of pure CTABr and 35 °C

The kinetic investigations on the effects of [4-ClC_{6}H_{4}CO_{2}Na] on $k_{obs}$ for the reaction of 0.10 M Pip, 0.20 mM PSH, in the presence of 0.006 M CTABr and different
concentrations of 4-ClC₆H₄CO₂Na (0.00–0.20 M) were carried out at constant 0.03 M NaOH, 35 °C and 370 nm. Similar observations were obtained by increasing the concentration of CTABr to 0.010 and 0.015 M. The values of $k_{obs}$ obtained are presented in Table 5.1.

5.3.2 Effect of [4-ClC₆H₄CO₂Na] on $k_{obs}$ for the reaction of Pip with PS⁻ at constant concentration of pure C₁₆E₂₀ and 35 °C

Several kinetic runs for the reaction of 0.10 M Pip with 0.20 mM PS⁻ at various concentrations of 4-ClC₆H₄CO₂Na (within the range of 0.00–0.20 M) and constant 0.030 M NaOH, and 0.001 M C₁₆E₂₀ were carried out. Similar observations were obtained by increasing [C₁₆E₂₀] to 0.003, 0.006, 0.008, 0.010, and 0.015 M. The observed data, $k_{obs}$ versus [4-ClC₆H₄CO₂Na] as well as $\delta_{app}$ and $A_\infty$, at [C₁₆E₂₀] = 0.001, 0.003, 0.006, 0.008, 0.010 and 0.015 M are presented, respectively, as Appendices G and H in the Appendix.

5.3.3 Effect of [4-ClC₆H₄CO₂Na] on $k_{obs}$ for the reaction of Pip with PS⁻ in the presence of mixed CTABr-C₁₆E₂₀ at 35 °C

Other sets of kinetic experiments were also conducted at constant 0.10 M Pip, 0.20 mM PS⁻ and 0.03 M NaOH in the presence of CTABr ([CTABr] = 0.006) at different [4-ClC₆H₄CO₂Na] (0.00–0.20 M). The concentrations of C₁₆E₂₀ were 0.006, 0.010 and 0.015 M. Similar results were obtained upon increasing [CTABr] to 0.010 and 0.015 M and the sketches of $k_{obs}$ against [4-ClC₆H₄CO₂Na] are presented in Figures 5.1, 5.2 and 5.3, respectively.

5.3.4 Rheological behavior of aqueous pure CTABr and mixed CTABr-C₁₆E₂₀ micelles in the presence of various [4-ClC₆H₄CO₂Na] at 25 and 35 °C

Two different rheometric investigations were conducted in the presence of pure CTABr (0.015 M) and mixed CTABr-C₁₆E₂₀ (0.015 M CTABr + 0.006 M C₁₆E₂₀)
micelles at different [4-ClC₆H₄CO₂Na]. Both were in aqueous solutions of 0.1 M Pip, 0.2 mM PSH and 0.03 M NaOH. The experiments were achieved at the steady shear rheological response, 25 and 35 °C. Various values of shear viscosity at various shear rates were determined and the results are presented in Figures 5.4 (a) and (b) (in the presence of pure CTABr) and Figures 5.5 (a) and (b) (in the presence mixed CTABr-C₁₆E₂₀).
Table 5.1: Values of observed pseudo-first-order rate constant, \( k_{\text{obs}} \), obtained for the piperidinolysis of \( \text{PS}^- \) at 0.006, 0.010 and 0.015 M CTABr and different \([4-\text{ClC}_6\text{H}_4\text{CO}_2\text{Na}]^\text{a}\).

<table>
<thead>
<tr>
<th>([\text{MX}]^b \text{ M})</th>
<th>([\text{CTABr}]^c = 0.006 \text{ M})</th>
<th>(0.010 \text{ M})</th>
<th>(0.015 \text{ M})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^4 \text{ k}_{\text{obs}}^d \text{ s}^{-1})</td>
<td>(10^4 \text{ k}_{\text{calcd}} \text{ s}^{-1})</td>
<td>(10^4 \text{ k}_{\text{obs}}^d \text{ s}^{-1})</td>
</tr>
<tr>
<td>0.000</td>
<td>24.1 ± 0.4\text{c}</td>
<td>21.2 ± 0.3\text{c}</td>
<td>21.9 ± 0.2\text{c}</td>
</tr>
<tr>
<td>0.001</td>
<td>23.2 ± 0.2</td>
<td>20.9 ± 0.4</td>
<td>20.8 ± 0.4</td>
</tr>
<tr>
<td>0.002</td>
<td>21.7 ± 0.4</td>
<td>19.8 ± 0.3</td>
<td>20.4 ± 0.2</td>
</tr>
<tr>
<td>0.004</td>
<td>26.7 ± 0.3</td>
<td>19.9 ± 0.3</td>
<td>20.4 ± 0.2</td>
</tr>
<tr>
<td>0.006</td>
<td>28.7 ± 0.4</td>
<td>20.9 ± 0.4</td>
<td>20.6 ± 0.1</td>
</tr>
<tr>
<td>0.008</td>
<td>39.5 ± 0.4</td>
<td>21.4 ± 0.3</td>
<td>20.7 ± 0.3</td>
</tr>
<tr>
<td>0.010</td>
<td>52.7 ± 0.5</td>
<td>25.3 ± 0.4</td>
<td>21.5 ± 0.2</td>
</tr>
<tr>
<td>0.015</td>
<td>84.5 ± 0.5</td>
<td>82.4\text{f}</td>
<td>36.7 ± 0.3</td>
</tr>
<tr>
<td>0.020</td>
<td>99.0 ± 0.7</td>
<td>103.1</td>
<td>48.1 ± 0.3</td>
</tr>
<tr>
<td>0.025</td>
<td>120.7 ± 0.7</td>
<td>118.4</td>
<td>54.9 ± 0.3</td>
</tr>
<tr>
<td>0.030</td>
<td>129.3 ± 0.9</td>
<td>130.2</td>
<td>63.8 ± 0.3</td>
</tr>
<tr>
<td>0.040</td>
<td>141.6 ± 1.3</td>
<td>147.3</td>
<td>82.4 ± 0.3</td>
</tr>
<tr>
<td>0.050</td>
<td>158.5 ± 1.7</td>
<td>159.0</td>
<td>96.0 ± 0.6</td>
</tr>
<tr>
<td>0.060</td>
<td>169.7 ± 1.8</td>
<td>167.6</td>
<td>112.4 ± 0.9</td>
</tr>
<tr>
<td>0.070</td>
<td>178.3 ± 1.3</td>
<td>174.1</td>
<td>120.8 ± 0.5</td>
</tr>
<tr>
<td>0.080</td>
<td>182.4 ± 1.6</td>
<td>179.2</td>
<td>128.8 ± 1.1</td>
</tr>
<tr>
<td>0.100</td>
<td>188.1 ± 1.9</td>
<td>186.8</td>
<td>142.7 ± 1.6</td>
</tr>
<tr>
<td>0.150</td>
<td>193.8 ± 1.2</td>
<td>197.6</td>
<td>160.8 ± 1.8</td>
</tr>
<tr>
<td>0.200</td>
<td>202.3 ± 2.4</td>
<td>203.3</td>
<td>166.5 ± 1.1</td>
</tr>
</tbody>
</table>

\[a\]\([\text{PSH}]_0 = 0.20 \text{ mM, } [\text{Pip}] = 0.10 \text{ M, } [\text{NaOH}] = 0.03 \text{ M, } \lambda = 370 \text{ nm and aqueous reaction mixture for each kinetic run contains 2\% v/v acetonitrile.}^b\] Total concentration of 4-ClC\_6H\_4CO\_2Na. \[\text{Total concentration of CTABr.}^c\] Observed pseudo first order rate constant. \[\text{Error limits are standard deviations.}^d\] Values of pseudo first order rate constant calculated from Eq. 3.13.
Figure 5.1: Plots showing the relationship between \( m_{obs} \) (where superscript “m” represents mixed micelles) and \([MX]\), \( MX = 4\text{-ClC}_6\text{H}_4\text{CO}_2\text{Na} \), for the reaction of Pip and \( \text{PS}^- \) at three different constant \([\text{CTABr}]_T + [\text{C}_{16}\text{E}_{20}]_T/M = 0.006 + 0.006 \) (●), 0.006 + 0.010 (♦) and 0.006 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant \( (k_{\text{calcd}}) \). Insert: The plots for magnified scale for the data points at lower values of \([MX]\).

Figure 5.2: Plots showing the relationship between \( m_{obs} \) (where superscript “m” represents mixed micelles) and \([MX]\), \( MX = 4\text{-ClC}_6\text{H}_4\text{CO}_2\text{Na} \), for the reaction of Pip and \( \text{PS}^- \) at three different constant \([\text{CTABr}]_T + [\text{C}_{16}\text{E}_{20}]_T/M = 0.010 + 0.006 \) (●), 0.010 + 0.010 (♦) and 0.010 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant \( (k_{\text{calcd}}) \). Insert: The plots for magnified scale for the data points at lower values of \([MX]\).
Figure 5.3: Plots showing the relationship between $^{m}k_{\text{obs}}$ (where superscript “m” represents mixed micelles) and [MX], MX = 4-CIC$_6$H$_4$CO$_2$Na, for the reaction of Pip and PS$^-$ at three different constant [CTABr]$_T$ + [C$_{16}$E$_{20}$]$_T$/M = 0.015 + 0.006 (●), 0.015 + 0.010 (♦) and 0.015 + 0.015 (▲), and 35 °C. The solid lines are drawn via the calculated values of the rate constant (k$_{\text{calcd}}$). Insert: The plots for magnified scale for the data points at lower values of [MX].
Figure 5.4: Graphs of shear viscosity (\(\eta\)) against shear rate (\(\dot{\gamma}\)) for the piperidinolysis of PS\(^-\) containing 0.015 M CTABr and [4-CIC6H4CO2Na]/M = (a) 0.008 (•) 0.015 (□) 0.030 (▲) 0.050 (♦) 0.080 (○) and 0.150 (◊) at 25 °C and (b) 0.008 (•) 0.015 (□) 0.030 (▲) 0.050 (♦) 0.080 (○) and 0.150 (◊) at 35 °C.
Figure 5.5: Graphs of shear viscosity ($\eta$) against shear rate ($\dot{\gamma}$) for the piperidinolysis of PS$^-$ containing 0.015 M CTABr, 0.006 M C$_{16}$E$_{20}$ and [4-ClC$_6$H$_4$CO$_2$Na]/M = (a) 0.008 (●) 0.015 (□) 0.030 (▲) 0.050 (●) 0.080 (○) and 0.150 (◊) at 25 °C and (b) 0.008 (●) 0.015 (□) 0.030 (▲) 0.050 (●) 0.080 (○) and 0.150 (◊) at 35 °C.
5.4 Discussion

5.4.1 Explanation of kinetic observations for the reaction of pip with PS in the presence of pure C_{16}E_{20} at various [4-ClC_{6}H_{4}CO_{2}Na] and 35 °C

The results obtained showed similar effect as explained in section 3.4.1 and the values of kinetic parameters are presented in Table 5.2.

Table 5.2: Values of kinetic parameters for the reaction of Pip and PS in the presence of 4-ClC_{6}H_{4}CO_{2}Na at different [C_{16}E_{20}]_{T} and 35 °C.

<table>
<thead>
<tr>
<th>[C_{16}E_{20}]_{T} (M)</th>
<th>k_{0, obs} (s^{-1})</th>
<th>k_{obs}^{MX (max)} (s^{-1})</th>
<th>%NSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>288</td>
<td>202</td>
<td>30</td>
</tr>
<tr>
<td>0.003</td>
<td>277</td>
<td>226</td>
<td>18</td>
</tr>
<tr>
<td>0.006</td>
<td>265</td>
<td>233</td>
<td>12</td>
</tr>
<tr>
<td>0.008</td>
<td>235</td>
<td>208</td>
<td>11</td>
</tr>
<tr>
<td>0.010</td>
<td>197</td>
<td>205</td>
<td>-</td>
</tr>
<tr>
<td>0.015</td>
<td>160</td>
<td>178</td>
<td>-</td>
</tr>
</tbody>
</table>

a[PSH]_{0} = 0.20 mM, [NaOH] = 0.03 M, [Pip] = 0.10 M, λ = 370 nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. bTotal concentration of C_{16}E_{20}. c{k}_{0, obs} = k_{obs} at [MX] = 0 (or average value of similar values of k_{obs} at various [MX]). d{k}_{obs}^{MX (max)} = k_{obs} at maximum value of [MX]. ePercent negative salt effect, %NSE caculated from Eq. 3.12.

5.4.2 Explanation of the effect of [4-ClC_{6}H_{4}CO_{2}Na] on k_{obs} for piperidinolysis of PS in the presence of pure CTABr and mixed CTABr-C_{16}E_{20} micelles

The values of observed pseudo first order rate constants, k_{obs}, for the reaction of 0.10 M Pip with 0.20 mM PS (at 35 °C and 370 nm) and varying values of [MX] (MX = 4-ClC_{6}H_{4}CO_{2}Na) in the presence of constant concentration of pure CTABr and mixed CTABr-C_{16}E_{20} were found to fit to Eq. 3.13. Various values of k_{0} were obtained in the presence of different concentrations of pure CTABr as well as mixed CTABr-C_{16}E_{20} at [MX] = 0 (Tables 5.3 and 5.4). To differentiate between the parameters determined in a
pure CTABr and mixed CTABr-C\textsubscript{16}E\textsubscript{20} micellar systems, a small letter “m” is used as a superscript to represent those obtained in the presence of mixed CTABr-C\textsubscript{16}E\textsubscript{20} micelles as elaborated in section 3.4.2. The values of [MX]\textsuperscript{op} obtained in the presence of both pure CTABr and mixed CTABr-C\textsubscript{16}E\textsubscript{20} are presented, respectively, in Tables 5.3 and 5.4.

The values of F\textsubscript{X/S} were obtained from Eq. 3.14 and are summarized in Tables 5.3 and 5.4 while the values of K\textsubscript{X/S} were determined by the use of Eq. 3.15 as in section 3.4.2. These calculated values of K\textsubscript{X/S} are shown in Table 5.3.

The relationship between the normalized values of K\textsubscript{X/S} (K\textsubscript{X/S}\textsuperscript{n} = F\textsubscript{X/S}/K\textsubscript{X/S}) and K\textsubscript{Br/S} (K\textsubscript{Br/S}\textsuperscript{n} = F\textsubscript{Br/S}/K\textsubscript{Br/S}) are discussed in section 3.4.2. The calculated values of K\textsubscript{X/S}\textsuperscript{n}, presented in Table 5.3, and the previously reported value of K\textsubscript{Br/S}\textsuperscript{n} (= 25 M\textsuperscript{-1}) (Khan, 1997a; Khan et al., 2000; Khan & Ismail, 2007), were used to calculate the values of relative counterion binding constants, K\textsubscript{X}\textsubscript{Br} (Khan, 2010) using Eq. 3.16. Similarly, the values of R\textsubscript{X}\textsubscript{Br} were calculated from Eq. 3.17 and the calculated values of (\textsuperscript{a}K\textsubscript{X/S})\textsuperscript{sp} and (\textsuperscript{a}K\textsubscript{Br/S})\textsuperscript{sp} in Table 5.3. These calculated values of K\textsubscript{X}\textsubscript{Br} or R\textsubscript{X}\textsubscript{Br} at [CTABr]\textsubscript{T} = 0.006, 0.010 and 0.015 M are also presented in Table 5.3 and their mean value (= 50.3) was found to be almost similar to the recently reported one (= 47.9) where the same inert organic salt (4-ClC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}Na) was used (Yusof & Khan, 2013). As explained in section 3.4.2, the values of \textsuperscript{m}K\textsubscript{X/S} could not be calculated due to the fact that the values of \textsuperscript{m}K\textsubscript{S}\textsuperscript{0} for mixed CTABr-C\textsubscript{16}E\textsubscript{20} surfactants are not available for the present study. Hence, Eq. 3.20 should be used for the calculation of \textsuperscript{m}K\textsubscript{X}\textsubscript{Br}. In addition, the values of \textsuperscript{m}R\textsubscript{X}\textsubscript{Br} were calculated using Eq. 3.21 and are presented in Table 5.3.

It is noteworthy that the values of \textsuperscript{m}K\textsubscript{X}\textsubscript{Br} or \textsuperscript{m}R\textsubscript{X}\textsubscript{Br} in the presence of mixed CTABr-C\textsubscript{16}E\textsubscript{20} micelles (Table 5.4) were found to be independent of Y (Y = [CTABr]/[C\textsubscript{16}E\textsubscript{20}]) and their mean value (= 22) is 2.3-fold lower than that in the presence of pure CTABr.
micelles (= 50). This significant decrease is, perhaps, due to the existence of the bulky hydrated headgroups of C$_{16}$E$_{20}$ which results in the hydration of cationic CTABr surfactant headgroups and consequently yielding relatively more hydrated bulky CTABr micellar phase. Thus, causing the larger sized hydrophilic head of C$_{16}$E$_{20}$ to cover the smaller sized headgroup of CTABr surfactants in mixed micelles (Gao et al., 2002).

5.4.3 Explanation of rheological behaviours for the reaction of Pip with PS$^-$ in the presence of pure CTABr and mixed CTABr-C$_{16}$E$_{20}$ micelles at various [4-ClC$_6$H$_4$CO$_2$Na]

From the rheometric information presented in Figures 5.4 (a) (at 25 °C) and (b) (at 35 °C), the two flow curves obtained at the lower value of [4-ClC$_6$H$_4$CO$_2$Na] (0.008 M) and the higher [4-ClC$_6$H$_4$CO$_2$Na] (0.15 M) show non-Newtonian fluid characteristics (mild shear thickening behaviors) at the higher values of shear rates, which may be due to “Taylor’s effect”. This is the characteristic features of spherical micelles, with relative lower values of shear viscosity ($\eta$) (Qiao et al., 2011). It has been recorded elsewhere (Acharya & Kunieda, 2006) that in a solution of ionic wormlike micelles containing certain salt, its viscoelastic nature could be changed at very high or low concentration of the added salt. However, the remaining four flow curves (at 0.015, 0.030, 0.050, and 0.15 M [4-ClC$_6$H$_4$CO$_2$Na]) with relatively higher values of $\eta$ revealed Newtonian fluid characteristics at the lower shear rate and show shear thinning behaviours at the relatively higher shear rate. This behavior is attributed to possibility of the presence of wormlike micelles (Lu et al., 2008). Figures 5.5 (a) and (b) shows a contrasting result in which all the flow curves exhibit a mild shear thickening behavior at a very low shear viscosity and high shear rate which is merely due to Taylor’s effect. This is a characteristic of spherical micelles and is directly related to the presence of a nonionic surfactant, C$_{16}$E$_{20}$ (Carver et al., 1996).
The plots of values of zero shear viscosity, $\eta_0$, against different concentrations of 4-ClC$_6$H$_4$CO$_2$Na are presented in Figure 5.6. Single symmetric maximum ($\eta_0 = 174.1$ mPas) was obtained in the presence of pure CTABr micelles ([CTABr]$_T = 0.015$ M and [C$_{16}$E$_{20}$]$_T = 0$) at [4-ClC$_6$H$_4$CO$_2$Na] = 0.03 M and 25 °C (□). Increasing the temperature to 35 °C (◇) provided similar results (maximum at [4-ClC$_6$H$_4$CO$_2$Na] = 0.03 M) with decrease in the value of $\eta_0$ ($\eta_0 = 21.4$ mPas). These maxima indicate the possible existence of wormlike micelles (Abdel-Rahem, 2008; Davies et al., 2006). As discussed earlier in this section, at very low [4-ClC$_6$H$_4$CO$_2$Na] (0.008 M) and high (0.15 M) with their respective values of $\eta_0$ as 1.00 and 1.97 mPas, there were characteristic features of spherical micelles (Acharya & Kunieda, 2006) when the temperature was 25 °C (□). Increasing the temperature to 35 °C (◇) has also provided similar results with the decrease in the values of $\eta_0$ from 1.00 and 1.97 mPas to 0.80 and 1.18 mPas, respectively.

In the presence of mixed CTABr-C$_{16}$E$_{20}$ ([CTABr]$_T = 0.015$ M and [C$_{16}$E$_{20}$]$_T = 0.006$ M), on the other hand, no maximum was observed at various values of [4-ClC$_6$H$_4$CO$_2$Na] (0.008, 0.015, 0.030, 0.050, 0.080, and 0.150 M) and both t 25 (Δ) and 35 °C (○).
Table 5.3: Values of empirical constants, ϑ, and $K^{X/S}$ obtained using Eqs. 3.13 and 3.14 with the $[MX]_0^{op}$ values for $MX = 4$-ClC$_6$H$_4$CO$_2$Na at different [CTABr]$_T$.

<table>
<thead>
<tr>
<th>[CTABr]$_T$ M</th>
<th>$10^4 k_0^e$ s$^{-1}$</th>
<th>$[MX]_0^{op}$ M</th>
<th>$10^3 \theta$ s$^{-1}$</th>
<th>$K^{X/S}$ M$^{-1}$</th>
<th>$F_{X/S}$</th>
<th>$K_{X/S}$ M$^{-1}$</th>
<th>$K^n_{X/S}$ M$^{-1}$</th>
<th>$K^Br_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006$^b$</td>
<td>24.1 ± 0.4$^d$</td>
<td>0.0065</td>
<td>22.2 ± 0.3$^d$</td>
<td>49.1 ± 2.4$^i$</td>
<td>0.69$^e$</td>
<td>2111$^f$</td>
<td>1456.8$^g$</td>
<td>58$^h$</td>
</tr>
<tr>
<td>0.010</td>
<td>21.2 ± 0.3</td>
<td>0.0100</td>
<td>21.4 ± 0.6</td>
<td>22.2 ± 1.6</td>
<td>0.67</td>
<td>1576</td>
<td>1056.1</td>
<td>42</td>
</tr>
<tr>
<td>0.015</td>
<td>21.9 ± 0.2</td>
<td>0.0129</td>
<td>21.6 ± 0.5</td>
<td>17.8 ± 1.1</td>
<td>0.67</td>
<td>1887</td>
<td>1264.2</td>
<td>51</td>
</tr>
</tbody>
</table>

$^a$[PSH]$_0$ = 0.20 mM, [NaOH] = 0.03 M, [Pip] = 0.10 M, λ = 370 nm and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile. $^b$Total concentration of CTABr $^c k_0 = k_{obs}$ at [MX] = 0. $^d$Limits of error signifies standard deviations. $^e F_{X/S} = \theta/k_{W}^{MX}$ where $k_{W}^{MX} = k_{W}^{2}[\text{pip}]_T = k_{obs}$ at [CTABr]$_T$ = 0 and the value of $k_{W}^{2}$, under such conditions is 0.322 M$^{-1}$s$^{-1}$. $^f K_{X/S} = K^{X/S}(1 + K_S^0[\text{CTABr}]_T)$, where $K_S^0 = 7 \times 10^3$ M$^{-1}$ (Khan & Arifin, 1996). $^g K^n_{X/S} = F_{X/S}K_{X/S}$. $^h K^Br_X = K^n_{X/S} / K^n_{Br/S}$, where $K^n_{Br/S} = 25$ M$^{-1}$ (Khan, 2010).
Table 5.4: Values of empirical constants, $m_0$ and $mK^{XS}$, obtained using Eqs. 3.13 and 3.14 with the $[MX]_0^{op}$ values for MX = 4-ClC₆H₄CO₂Na at different concentrations of mixed CTABr-C₁₆E₂₀.

<table>
<thead>
<tr>
<th>[CTABr]$_T$ M</th>
<th>[C₁₆E₂₀]$_T$ c</th>
<th>$10^4 m_0$ d</th>
<th>$m[MX]_0^{op}$ M</th>
<th>$10^3 m_0$ e s⁻¹</th>
<th>$mK^{XS}$ M⁻¹</th>
<th>$mF_{X/S}$</th>
<th>$m n K^{XS}$ M⁻¹</th>
<th>$m n K^{Br/SH}$ M⁻¹</th>
<th>$mK_X$ or $mR_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006 b</td>
<td>0.006</td>
<td>25.0 ± 0.3 e</td>
<td>0.00350</td>
<td>20.4 ± 0.4 e</td>
<td>36.1 ± 2.0 e</td>
<td>0.85 f</td>
<td>30.7 e</td>
<td>1.4 f</td>
<td>21.9 f</td>
</tr>
<tr>
<td>0.006</td>
<td>0.010</td>
<td>30.6 ± 0.4</td>
<td>0.00182</td>
<td>20.5 ± 0.2</td>
<td>35.0 ± 1.3</td>
<td>1.06</td>
<td>37.1</td>
<td>2.2 f</td>
<td>16.9</td>
</tr>
<tr>
<td>0.006</td>
<td>0.015</td>
<td>31.0 ± 0.5</td>
<td>0.00109</td>
<td>17.0 ± 0.2</td>
<td>44.6 ± 1.7</td>
<td>0.92</td>
<td>41.0</td>
<td>1.8 f</td>
<td>22.8</td>
</tr>
<tr>
<td>0.010</td>
<td>0.006</td>
<td>24.9 ± 0.4</td>
<td>0.00223</td>
<td>24.3 ± 0.8</td>
<td>16.8 ± 1.1</td>
<td>1.01</td>
<td>17.0</td>
<td>1.0 f</td>
<td>17.0</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>31.3 ± 0.5</td>
<td>0.00201</td>
<td>16.6 ± 0.2</td>
<td>27.4 ± 0.8</td>
<td>0.86</td>
<td>23.6</td>
<td>1.1 f</td>
<td>21.5</td>
</tr>
<tr>
<td>0.010</td>
<td>0.015</td>
<td>26.1 ± 0.4</td>
<td>0.00233</td>
<td>18.8 ± 0.2</td>
<td>23.0 ± 0.6</td>
<td>1.02</td>
<td>23.5</td>
<td>0.9 f</td>
<td>26.1</td>
</tr>
<tr>
<td>0.015</td>
<td>0.006</td>
<td>24.7 ± 0.2</td>
<td>0.01065</td>
<td>18.6 ± 0.4</td>
<td>18.7 ± 1.1</td>
<td>0.78</td>
<td>14.6</td>
<td>0.8 f</td>
<td>18.3</td>
</tr>
<tr>
<td>0.015</td>
<td>0.010</td>
<td>25.7 ± 0.3</td>
<td>0.00820</td>
<td>19.4 ± 0.8</td>
<td>17.0 ± 1.7</td>
<td>1.00</td>
<td>17.0</td>
<td>0.6 f</td>
<td>28.6</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
<td>26.9 ± 0.3</td>
<td>0.00820</td>
<td>18.7 ± 0.4</td>
<td>18.3 ± 0.9</td>
<td>0.98</td>
<td>17.9</td>
<td>0.8 f</td>
<td>22.4</td>
</tr>
</tbody>
</table>

Footnote: $a$ and $b$ are the same as in Table 5.3. *Total concentration of C₁₆E₂₀. $d m_0 = k_{obs}$ at [MX] = 0. *Limits of error signifies standard deviations. $f mF_{X/S} = m_0^{obs} / mK^{W}$; with $mK^{W} = mK^{obs} (= mK^{obs}_{[Pip]}_T) = 240 \times 10^{-4}$, 193.2 $\times 10^{-4}$ and 184.2 $\times 10^{-4}$ s⁻¹ at constant [C₁₆E₂₀]$_T$ (0.006, 0.010 and 0.015 M [C₁₆E₂₀], respectively) and [MX] = [CTABr] = 0. $g n mK^{XS} = mF_{X/S} mK^{XS}$ for MX = NaBr. *Data are obtained from reference (Fagge et al., 2016). $i mK^{Br} or mR_X = mK^{XS} / mK^{Br/S}$.
Figure 5.6: Plots of zero shear viscosity ($\eta_0$) against [4-ClC$_6$H$_4$CO$_2$Na] at a constant shear rate ($\dot{\gamma}$) with 0.015 M CTABr in the absence of C$_{16}$E$_{20}$ at 25 °C (□) and 35 °C (○), and the presence of 0.006 M C$_{16}$E$_{20}$ at 25 °C (△) and 35 °C (○).

5.5 Conclusion

The mean values of relative counterion (4-ClC$_6$H$_4$CO$_2$) binding constants ($K_X^{Br}$ or $R_X^{Br}$) in the present study ($K_X^{Br}$ or $R_X^{Br}$ = 50) and that of previously reported article ($K_X^{Br}$ or $R_X^{Br}$ = 47) for aqueous CTA$^+$/4-ClC$_6$H$_4$CO$_2$ is reduced to more than $\frac{1}{2}$-fold ($mK_X^{Br}$ or $mR_X^{Br}$ = 22) when C$_{16}$E$_{20}$ (0.006 to 0.015 M) is added to the solution (CTA$^+$/C$_{16}$E$_{20}$/4-ClC$_6$H$_4$CO$_2$). Though wormlike micelles were found in aqueous CTA$^+$/4-ClC$_6$H$_4$CO$_2$ ([CTABr]$_T$ = 0.015 M) solution, spherical micelles also existed at very high and low concentrations of 4-ClC$_6$H$_4$CO$_2$Na (which were revealed in CTA$^+$/C$_{16}$E$_{20}$/4-ClC$_6$H$_4$CO$_2$ solution). The significantly new findings in this chapter are: (i) $K_X^{Br}$ or $R_X^{Br}$ for 4-ClC$_6$H$_4$CO$_2$ in aqueous CTABr micellar solution could be reduced when certain amount of nonionic surfactant with larger sized hydrophilic tail is added (ii) 4-ClC$_6$H$_4$CO$_2$-induced CTABr micellar structural growth and viscoelasticity could skilfully be managed, not only by changing the counterion, $X^-$, (for instance 4-ClC$_6$H$_4$CO$_2$), pH, etc.,
but also by the addition of nonionic surfactant, such as C\textsubscript{16}E\textsubscript{20}. It is, therefore, concluded that the addition of small amount of C\textsubscript{16}E\textsubscript{20} influences, significantly, the CTABr micellar structural transition.
CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusion

The present research highlights the effect of polyethylene glycol hexadecyl ether, a nonionic surfactant (C_{16}E_{20}), on the relative counterion binding constants, $K_X^{Br}$ or $R_X^{Br}$, and counterion-induced hexadecyltrimethylammonium bromide, CTABr, micellar structural growth. The semi empirical kinetics technique was used to correlate the values of $K_X^{Br}$ or $R_X^{Br}$ with the micellar structural behaviours. The data are ascertained by the rheometric results obtained in the second part of the experiments. The nonionic surfactant, as extensively discussed in chapter 3, 4, and 5, has been found to play an important role in the decrease of the values of $K_X^{Br}$ or $R_X^{Br}$, as well as changes in the CTABr micellar structure.

The mean values of $K_X^{Br}$ or $R_X^{Br}$, for CTABr/MX/H_{2}O, in the presence of different halo-substituted benzoate salts with counterions, $X = 2$-NaOC_{6}H_{4}CO_{2}^{-}, 3,5-Cl_{2}C_{6}H_{3}CO_{2}^{-}, and 4-ClC_{6}H_{4}CO_{2}^{-}$ are, respectively, 42, 198, and 50. The mean values of $K_X^{Br}$ or $R_X^{Br}$ for CTABr/C_{16}E_{20}/MX/H_{2}O significantly dropped to 16 ($X = 2$-NaOC_{6}H_{4}CO_{2}^{-}), 78 (for $X = 3,5$-Cl_{2}C_{6}H_{3}CO_{2}^{-}), and 22 (for $X = 4$-ClC_{6}H_{4}CO_{2}^{-}) due to the presence of nonionic surfactant, C_{16}E_{20}. The rheometric investigations have been used in ascertaining the viscoelastic behaviours and structure of CTA$^+$/X$^-$/H_{2}O micelles at [CTABr]$_T$ = 0.015 M, and the existence of wormlike micelles were obtained in the absence of C_{16}E_{20}. But the CTA$^+$/C_{16}E_{20}/X$^-$/H_{2}O solution showed the presence of spherical micelles at [CTABr]$_T$ = 0.015 M and [C_{16}E_{20}]$_T$ = 0.006 M. It is now concluded that addition of a relatively small amount of nonionic surfactant (for instance [C_{16}E_{20}]$_T$ $\geq$ 0.006 M) to an aqueous solution of cationic CTABr surfactant could be a method of to change the CTABr micellar structure.
The new and interesting outcomes of this research work are; (i) The experimentally determined values of $K_X^{Br}$ or $R_X^{Br}$ for counterions $2$-$NaOC_6H_4CO_2^-$, $3,5$-$ClC_6H_4CO_2^-$, and $4$-$ClC_6H_4CO_2^-$ in the presence of mixed cationic-nonionic surfactants (CTABr-$C_{16}E_{20}$)–values were found to be significantly lower than those determined in the presence of pure CTABr micelles. (ii) The observations noted the quantitative correlation of the values of $K_X^{Br}$ or $R_X^{Br}$ obtained with the counterions-induced CTABr micellar structural change from wormlike (in $CTA^+/X^-/H_2O$ solution) to spherical (in $CTA^+/C_{16}E_{20}/X^-/H_2O$ solution). This correlation has been used to predict the cationic CTABr micellar structure (at $[CTABr]_T$ range of $0.006$–$0.015$ M) and its counterion-induced structural changes in the presence of $0.006$–$0.015$ M $[C_{16}E_{20}]_T$ at different values of certain inert salts. It has also been noted, perhaps for the first time, that the values of $K_X^{Br}$ or $R_X^{Br}$ are quantitatively correlated to the counterion-induced CTABr micellar structural changes (and ascertained by the rheometric evidence) in the presence of a nonionic surfactant, $C_{16}E_{20}$.

6.2 Future Directions

The present research focused on the influence of one nonionic surfactant on the relative counterion binding constant of cationic micelles and their induced micellar growth. It has also limited to three benzoate salts. The experiments conducted were kinetic and rheometric measurements using respectively, UV-Visible spectrophotometer and rheometer

It is recommended that the direction of future work should be towards the addition of other nonionic surfactants, with similar properties to $C_{16}E_{20}$ (those whose hydrophilic group is a polyethylene glycol chain), on CTABr micellar system. Studies on relative counterion binding constants, in the presence of different surfactant-cosurfactant combination, are also highly recommended. Different experiments such as cryo-TEM, SANS, etc and other benzoate salts should also be included in future studies.
REFERENCES


LIST OF PUBLICATIONS AND PAPERS PRESENTED

Journal Articles:


International Conferences:
