Cooperative Assembly of Ionic Liquid and Surfactants for the Determination of CMC of Nonionic Surfactants by Conductometry

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Cooperative Assembly of Ionic Liquid and Surfactants for the Determination of CMC of Nonionic Surfactants by Conductometry

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Abstract

A simple and rapid method for the determination of Critical Micelle Concentration of nonionic surfactants/block copolymers by ionic conductivity measurements has been proposed. In this method, a water soluble ionic liquid (1-butyl pyridinium chloride) is used to probe conductivity. Though the ILs employed here do not undergo any self association by itself at the concentrations studied, it takes part in micelle formation in the presence of other surfactants through a cooperative assembly process. This leads to remarkable changes in the conductance of the solution as a function of surfactant concentration which aids in determining the CMC of nonionic surfactants conductometrically. The CMC values are found in excellent agreement with those obtained by the other conventional methods. This method is validated for surfactants with varying molecular weights and having different hydrophobic parts. The concentration of IL was optimized using Small Angle Neutron Scattering, Dynamic Light Scattering and $^1$H-Nuclear Magnetic Resonance.

Keywords: Critical Micelle Concentration, Nonionic Surfactant, Block Copolymers, Conductivity Method, Surface Tension
1. Introduction

Surfactants or Surface Active Agents, are amphiphiles consisting of polar and apolar groups which have dual affinity for water and oil. The surfactant molecule leads to formation of aggregates in water, known as Micelles. The Critical Micelle Concentration (CMC) is the ‘benchmark concentration’ above which appreciable number of aggregates are formed, knowledge of which is essential for desired application of surfactants. At CMC, drastic changes in physical properties\(^1-^3\) are observed and there are numerous methods for determining CMC by measuring these properties. The CMC determination methods are categorized as direct and indirect methods. In the former case, change in physical properties\(^1-^3\) (surface tension,\(^4,^5\) electrical conductivity,\(^6,^7\) refractive index,\(^8,^9\) light scattering,\(^10\) etc.) are measured as a function of concentration, while in later case, probes or tracers are used to measure change in their properties (dye solubilization, fluorescence spectrophotometry etc.).\(^14-^25\) Surface tension (ST), dye solubilization and fluorescence spectrophotometry are most widely used for determination of CMC of surfactants amongst the aforementioned methods. It has been observed that direct methods are superior to indirect method in order to determine CMC values precisely. This is because of the fact that dye solubilization and fluorescence spectrophotometry require the use of a dye and fluorescence probe as tracer for CMC determination; which actually induces micelle formation and reduction of CMC values for surfactants.\(^26\)

Surface tension (ST) and ionic conductivity measurements are the most popular methods for determining CMC of surfactant solutions. Surface tension is extensively used technique since the surface tensiometer is easy to operate, making evaluation of CMC simple. Moreover, ST is suitable for all kind of surfactants (nature), whereas the ionic conductivity method though extensively employed, is limited to ionic surfactant in aqueous and non-aqueous media
In ionic conductivity method, a clear slope change is observed in the specific conductivity ($\kappa$) Vs concentration ($C$) plot which corresponds to CMC. It is well known that conductance method is not appropriate for the CMC determination of nonionic surfactants, still Svitova and Pletnev$^{30}$ used conductivity method for the nonionic surfactant solutions. They observed that a change in slope of straight line in $\kappa$ Vs $C$ plot was not clear. The inflection point becomes clear when an electrolyte is added to the solution of nonionic surfactants which normally affects the CMC value of the same. But except the conductivity method all the major techniques used for CMC determination require sophisticated equipments. Owing to the above mentioned issues, it is desirable to find or design a tracer or probe which has negligible effect on CMC and can be used for CMC determination of nonionic surfactants by conductivity method.

For this purpose, Ionic Liquid (IL) may be a promising candidate, as it possesses good electrical conductivity and tunable structural dependent properties.$^{31,32}$ Recently, ILs have attracted considerable interest due to their unique features like, low vapor pressure, wide liquid range, good conductivity and large electrochemical window.$^{33}$ These properties make it suitable to apply in the field like catalysis, electrochemistry, formation of metal nanostructure, sensor etc.$^{34-36}$ The variety of applications show that ILs offer a high solvating, yet non-coordinating medium in which a number of organic and inorganic solutes may be dissolved which make it an appropriate media to work with.

The aim of the proposed work is two-fold, where initially we look forward to develop a cooperative assembly of IL with surfactant and subsequently using this assembly we determine CMC of non-ionic surfactants by conductivity method. The present unique method is validated for surfactants with different molecular weights having variety of hydrophobic part along with different hydrophobic/hydrophilic ratio. The CMC values obtained by this
method were also compared with that obtained by other methods. SANS, DLS and $^1$H-NMR are used to understand the interaction between IL and surfactant as well as its effect on micellar size and shape.

2. Experimental

The detailed specifications of all nonionic surfactants/block copolymers are given in Table 1. The CMC values of nonionic surfactants, Triton X-100 (>99% purity, Fluka), Brij-98 (>99% purity, Sigma-Aldrich), nonionic silicon surfactants (Degussa, Germany) and Amphiphilic block copolymers Pluronics® F127, P123, P105 (Sigma-Aldrich) and (EO-BO-EO) B – 1 and B – 2 (Dow Corning Chemicals, USA) were determined at 30 °C ± 0.1 °C. The ionic liquid $\text{C}_4\text{PyCl}$ (99.99+, Merck) was used as a probe for the determination of CMC of all above mentioned surfactants. All the chemicals were used as received. All surfactant solutions were prepared in de-ionized water having conductivity ~5 \times 10^{-6} \text{ S cm}^{-1} to which constant volume of $\text{C}_4\text{PyCl}$ was added in all solutions in such a way that the net concentration of $\text{C}_4\text{PyCl}$ becomes 15 mM. The conductivity of the aqueous surfactant solutions in presence of IL were measured using digital conductivity meter (Equiptronics, India). The conductivity cell (cell constant, 0.1 cm$^{-1}$) was immersed in surfactant solutions which were kept in constant temperature (~30 °C) water bath. The measurements were repeated three times for each concentration of surfactants. The surface tensions of all solutions were also measured by surface tension using a tensiometer (Data Physics, Germany) at the same temperature. The specific and relative viscosities for surfactants/polymers with and without IL were measured using Ubbelohde Viscometer in constant temperature bath at 30°C.

SANS measurements were carried out on the surfactant solutions prepared in D$_2$O at the SANS facility at DHRUVA reactor, Trombay. The mean incident wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15 \%$. The scattering was measured in the scattering vector ($q$) range of 0.017–0.3 Å$^{-1}$. 
The measured SANS data were corrected for the background, empty cell contributions, and transmission and were placed on an absolute scale using standard protocols. The detailed data analysis were made using core-shell hard sphere model.\textsuperscript{37,38} DLS measurements were carried out in the H\textsubscript{2}O medium using a Malvern 4800 Autosizer with 7132 digital correlator. The light source was an argon ion laser operated at 514.5 nm with a maximum output power of 2 W. The average decay rate was obtained by analyzing the electric field autocorrelation function, $g_1^f(\tau)$ vs. time data using a modified cumulants method as has recently been proposed.\textsuperscript{39} The apparent equivalent hydrodynamic radii of the micelles were calculated using the Stokes-Einstein relationship. All NMR experiments were conducted on a Bruker Avance 400 spectrometer at a frequency of 400.13 MHz in D\textsubscript{2}O and TMS as internal standard.

3. Result and Discussion

3.1 Optimization of Ionic Liquid Concentration for CMC determination:

For the utilization of IL (charge entity) as a tracer for CMC determination of nonionic surfactants by conductometry, the selection of IL and its concentration is crucial. The concentration and nature of IL have to be optimized in such a way that it will make a cooperative assembly of IL with nonionic surfactants. ILs have a tendency to undergo aggregation at much higher concentration than that of conventional ionic surfactant in various solvents.\textsuperscript{40} From our recent study we found that pyridinium cation with butyl chain have almost negligible effect on the micelles of Pluronic block copolymer P123. In addition to this, C\textsubscript{4}PyCl was unable to form stable aggregates while IL with higher alkyl chain form aggregates at room temperature.\textsuperscript{40,42} Because the hydrophobicity of lower chain ILs are not sufficient enough to cause self association. Preliminary conductivity measurements of such ILs in the presence of P123 solution showed remarkable changes in the electrical...
conductivity. This prompted us to explore the use of appropriate IL as probes for CMC of nonionic surfactants via ionic conductivity measurement. For the CMC determination by conductometry, we have selected pyridinium based IL with butyl chain. The concentration of IL is selected in such a way that it falls very well below the CMC value of IL surfactant and has negligible effect on morphology of micelles. Hence, IL should have very less interaction with hydrophobic/hydrophilic part of surfactants and will only charge the micelles. Due to this, it has an impact on conductivity of IL in pre-micellar and micellar phase. In order to optimize the concentration of IL (C₄PyCl), we started with P123 (EO₂₀-PO₇₀-EO₂₀) system which is well known for formation of well organized spherical micelles. The SANS and DLS methods were used to measure the effect of IL on morphology of P123 micelles in aqueous solutions while NMR study gives an idea about interaction of IL with surfactants. Figure 1 represent the SANS curves for 15%w/w of P123 solutions (well above from CMC value i.e. 0.015% w/w) in presence of 100 mM C₄PyCl at 30 °C. Figure 1 reveals that upon addition of 100 mM IL, there was no appreciable change in SANS profile which in turn can be easily gauged by any change in peak position as well as intensity. The SANS curves were fitted to hard sphere core-shell model and the parameters obtained from the fits are reported in Table 2. It is evident from the data in Table 2 that up to 100 mM concentration of IL, there is no change in size and shape of P123 micelles. This reveals that the structures of the aggregates are seldom affected by the addition of IL. The same was also confirmed with the help of DLS measurements. The plots of the intensity correlation function for 15%w/w P123 in absence and presence of IL (50 mM) at a scattering angle of 90° are illustrated in Figure 2. It can be seen from figure that the addition of 50mM IL was unable to cause any shift in the correlation function vs time plot which manifests pristine micellar morphology of P123. Analysis of the same is carried out using the regularized non-negatively constrained method, CONTIN which shows a unimodal distribution of relaxation rate. The
hydrodynamic radius \((R_h)\) parameter obtained by this method are depicted in column 7 of Table 2 which clearly shows negligible effect of 50 mM IL concentration on the P123 micelles. From the above measurements and inferences, we choose 15 mM of IL as an appropriate concentration for CMC determination using conductometry.

In order to know the interaction and position of IL in micelles, the concentration dependent \(^1\text{H} \text{NMR}\) spectra for P123 block copolymer in presence of 15 mM C\(_4\)PyCl are measured. (Please see supporting information Figure S1). The concentration of block copolymers were selected in such a way that they were below and above CMC values. From the \(^1\text{H} \text{NMR}\) spectra, the \(\delta_{ppm}\) values at 4.80, 3.61, 3.49, 1.24 corresponds to HDO, EO –\(\text{CH}_2–\), PO –\(\text{CH}_2–\), PO –\(\text{CH}_3\), respectively which are in good agreement with previous assignments\(^{45}\) and the remaining signals are attributed to IL.\(^{42}\) The presence of different multiplets at lower concentration (below CMC) of P123 is because of efficient motion of polymeric chain which indicates that even in presence of IL, all segments of the solvated polymer can move freely. This has marked effect on the conductivity of IL. When the concentration is increased above a certain value (CMC), the chemical shifts of PO, PO –\(\text{CH}_2–\) / –\(\text{CH}_3\) slightly shifted towards downfield, while of PO –\(\text{CH}–\) shifted slightly towards upfield. This indicates that PPO domain of P123 micelle undergoes usual interaction with water\(^{45}\) and is not affected by presence of IL. In order to outrace the location of IL in micelles we have monitored the change in chemical shifts of terminal methyl (–\(\text{CH}_3\)) group of butyl chain as well as aromatic ring hydrogen of head group of IL (Figure 3). Figure 3 reveals increase in the chemical shifts of both types of hydrogen. The observed downfield shift of the terminal \(\text{–CH}_3\) of butyl chain protons discloses that the IL is associated with the P123 micelles through a cooperative interaction. Further, the downfield shift of the proton signals indicates that the IL is located in the PEO shell of the micelle, rather than in the PPO core. The association of IL with P123
micelles is further supported from the significant broadening of the NMR signals. The broadening of the signals arises from the restricted rotation of IL in P123 micelles, as it is associated with the aggregates. Thus, addition of C\textsubscript{4}PyCl (below 100mM) into micelle of nonionic block copolymers/surfactants in aqueous solution produces cooperative association of the IL with P123 micelles. As this cooperative association exists only when the micelles are formed, such association can lead to changes in the mobility of IL, it is expected that such IL can be utilized for CMC determination of nonionic surfactants by conductivity measurements.

3.2 CMC determination by Conductometry:

As discussed in experimental section, all surfactant solutions were prepared in aqueous solution of 15 mM C\textsubscript{4}PyCl and have specific conductivity 948 µScm\textsuperscript{-1} at 30 °C. The conductivity of C\textsubscript{4}PyCl solution changes upon addition of nonionic surfactants. The conductivity curves of C\textsubscript{4}PyCl in presence of increasing amount of nonionic surfactants were studied and found to change markedly like in surface tension curves (ST vs conc.). The specific conductivity versus concentration plots for the aqueous solution of surfactants (having different hydrophobic groups) in presence of 15 mM C\textsubscript{4}PyCl are shown in Figure 4. For the comparison purpose we have put surface tension data of the same systems in the Figure 4. A perusal of figure divulges marked change in conductivity of C\textsubscript{4}PyCl until the formation of stable micelles (i.e. complete aggregation of surfactant molecules). The conductivity remains almost constant upon further addition of surfactant above the CMC values. The concentration at which conductivity attained the constant values is equal to CMC. The exact CMC values are obtained by plotting the conductivity of the C\textsubscript{4}PyCl-surfactant mixtures Vs concentration of the surfactants. The obtained CMC values for different surfactants from conductivity method along with surface tension and other methods are
depicted in Table 3. It can be clearly seen that the CMC values obtained by variation in conductivity of C₄PyCl is in good agreement with the literature data as well as those obtained by surface tension method. Unlike other additive (indirect) methods where dyes or organic molecules are used as probe, this method does not cause any effect on the micellization processes. In order to check versatility of this method, we have selected block copolymers/surfactants in such a way that they have different hydrophobic moieties and industrially important surfactants like Triton X-100, Brij-98 are also used. The change in conductivity of C₄PyCl may be due to restriction in the motion of IL. As discussed in previous section, through NMR study we found that the IL molecules are located at hydrated PEO/PPO interface which restrict the motion of IL molecules which in turn decreases the conductivity of the IL.

It is very well documented that, Pluronic block copolymers in surface tension curves show two distinct break points and generally second break point is considered as the CMC value. Alexandridis et al reasoned that Pluronic EPE copolymer molecules at very low copolymer bulk concentration adsorbs at the air/water interface in an extended conformation. And when the concentration increases, the interface gets fully covered with copolymer molecules, thus changing the extended conformation to an inverted ‘∩’. The two ends of inverted ‘∩’ blocks its contacts with water while the middle hydrophobic part protrudes into the air. This change in conformation would manifest as first break point in surface tension-concentration plots. Other indirect methods like dye solubilization, cyclic voltammetry, fluorescence spectroscopy etc. are insensitive for evaluating double break points. Figure 4(a) and S2 (a & b) (supporting information) portrait the formation of double break point in Pluronic block copolymers. The figures reveal that the first break point observed by conductivity method is also in good agreement with the one obtained by ST method, indicating that our proposed
The double break point in conductivity measurements can be explained as follows: the quaternary ammonium ion of C₄PyCl is known for making coordination bonds with etheric oxygen of PEO and PPO and as we know that at very low polymer concentration, hydrophobic part will reside at the air/water interface thus it is less available in the bulk solution. This will result into rare chances of interaction of quaternary ions with lone pair of oxygen from PPO providing free mobility to ionic species of IL leading to less change in conductivity. At higher polymeric concentration, the availability of PPO is maximum at air/water interface than PEO. Due to this the ions of IL will interact with PPO which ultimately reduces the mobility. Furthermore, after achieving CMC, the PPO part will undergo dehydration and interaction between highly hydrated PEO and IL may only exist, which leads to restriction in the motion of ionic species and thus conductivity. Therefore, we can say that the proposed method is simple as well as sensitive towards such kind of changes along with the determination of CMC values of nonionic surfactants where sophisticated instrumentation is not required. It is worth to mention that the viscosity effect on conductivity of IL has not been considered in the change of conductivity as a function of concentration of block copolymers/surfactants because the variation in viscosity of polymer with concentration is not prominent. (Please see Figure S4)

Conclusions

A simple and novel method has been devised for the determination of CMC values for nonionic surfactants using conductometry where water soluble C₄PyCl was used for making cooperative assembly with nonionic surfactants/block copolymers. Selection of IL and optimization of its concentration was carried out using SANS and DLS measurements. ¹H NMR measurements gave an insight into the location as well as interaction of IL inside the micelles of surfactants. From these experiments we have observed that IL does not affect the
morphology of micelles via strong interaction with hydrophobic or hydrophilic part of the surfactant. This method was validated for various nonionic surfactants having different hydrophobic parts and hydrophobic/hydrophilic ratio. The CMC values obtained by this method are in good agreement with the one obtained by other versatile methods and its sensitivity was proved by observing double break points in the Pluronic block copolymer system. Thus we can say that the conductivity method can be employed for the determination of CMC of nonionic surfactants using IL as conducting probe.

Acknowledgement

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Captions to Figures

**Figure 1** SANS spectra of 15%(w/w) P123 in D₂O and 100mM C₄PyCl

**Figure 2** Representative plot of the intensity correlation function for 50 mM C₄PyCl with 15%(w/w) P123 at a scattering angle of 90°. The solid line is a fit to the data using the method of CONTIN.

**Figure 3** Aggregation of Pluronic in presence of 15mM C₄PyCl by ¹H NMR Spectroscopy. δ ppm is the observed chemical shift (a) for aromatic proton (b) for the proton of the terminal methyl unit.

**Figure 4** Specific conductance vs. concentration of surfactants at 30°C, (a) P123, (b) B – 2, (c) Triton X-100, (d) Brij – 98 and (e) SS – 1 (conductivity of 15 mM C₄PyCl is 948 µS/cm² in water)
Table 1 Molecular formula, molecular weight and % of EO for various surfactants/block copolymers

<table>
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<tr>
<th>Sr. No.</th>
<th>Surfactant/ Block copolymer</th>
<th>Formula</th>
<th>Mol. wt. gm.mol⁻¹</th>
<th>% EO</th>
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<tr>
<td>1</td>
<td>P123</td>
<td>(EO)₂₀(PO)₇₀(EO)₂₀</td>
<td>5750</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>P105</td>
<td>(EO)₉₀(PO)₆₀(EO)₉₀</td>
<td>6500</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>F127</td>
<td>(EO)₃₇(PO)₅₆(EO)₃₇</td>
<td>12600</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>B – 1</td>
<td>C₄H₉O-(BO)ₙ-(EO)ₘ-OH</td>
<td>1500</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m = 16, n = 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B – 2</td>
<td>HO-(EO)ₘ-(BO)ₙ-(EO)ₘ-OH</td>
<td>5000</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m = 43, n = 14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Triton X - 100</td>
<td>C₈H₁₇-C₄H₄-O(CH₂CH₂O)₉.₅H</td>
<td>625</td>
<td>80</td>
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<tr>
<td>7</td>
<td>Brij - 98</td>
<td>C₁₈H₃₅-(OCH₂CH₂)ₙOH, n~20</td>
<td>1149</td>
<td>80</td>
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<td>8</td>
<td>SS – 1</td>
<td></td>
<td>4360</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>SS - 2</td>
<td><img src="image" alt="SS-2 Structure" /></td>
<td>5600</td>
<td>75</td>
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For SS – 1 m = 5, n = 13, x = 12, y = 0
For SS – 2 m = 5, n = 20, x = 10, y = 4

EO = Ethylene Oxide, PO = Propylene Oxide, BO = Butylene Oxide
Table 2 Values of Core radius, $R_C$, Shell thickness, $R_S$, Hard sphere radius, $R_{HS}$, Polydispersity, $\sigma$, Volume fraction, $\phi$, Hydrodynamic radius, $R_h$, for 15 % (w/w) aqueous solutions of P123 in presence and absence of C$_4$PyCl

<table>
<thead>
<tr>
<th>System</th>
<th>$R_C$ (Å)</th>
<th>$R_S$ (Å)</th>
<th>$R_{HS}$ (Å)</th>
<th>$\sigma$</th>
<th>Volume fraction $\phi$</th>
<th>$R_h$ (Å)$^a$</th>
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<tr>
<td>P123 + D$_2$O</td>
<td>36.3 ± 0.2</td>
<td>6.8 ± 0.1</td>
<td>79.7 ± 0.3</td>
<td>0.49</td>
<td>0.152</td>
<td>94.5 ± 0.4</td>
</tr>
<tr>
<td>P123 + 50 mM C$_4$PyCl</td>
<td>36.2 ± 0.2</td>
<td>6.7 ± 0.1</td>
<td>79.5 ± 0.3</td>
<td>0.49</td>
<td>0.153</td>
<td>94.1 ± 0.4</td>
</tr>
<tr>
<td>P123 + 100 mM C$_4$PyCl</td>
<td>36.8 ± 0.2</td>
<td>6.7 ± 0.1</td>
<td>79.2 ± 0.3</td>
<td>0.48</td>
<td>0.157</td>
<td>93.1 ± 0.3</td>
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$^a$ Obtained from DLS measurements
Table 3 Critical Micelle Concentration of surfactants and block copolymers obtained from Conductivity method and surface tension method at 30°C.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Critical Micelle Concentration (g.dl⁻¹)</th>
<th>Surface tension</th>
<th>Conductivity</th>
<th>Lit.</th>
<th>Ref.</th>
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<tr>
<td>P123</td>
<td>5.7±0.3 × 10⁻³</td>
<td>5.4±0.3 × 10⁻³</td>
<td>5.0 × 10⁻³[a]</td>
<td></td>
<td>[48]</td>
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<tr>
<td>P105</td>
<td>3.7±0.2 × 10⁻²</td>
<td>3.5±0.2 × 10⁻²</td>
<td>2.5 × 10⁻²[a]</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>F127</td>
<td>4.0±0.2 × 10⁻²</td>
<td>3.6±0.2 × 10⁻²</td>
<td>3.9 × 10⁻²[ba]</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>B - 1</td>
<td>1.9±0.1 × 10⁻³</td>
<td>1.5 ±0.1 × 10⁻³</td>
<td>2.2 × 10⁻³[ba]</td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>B - 2</td>
<td>2.5±0.1 × 10⁻²</td>
<td>2.3±0.1 × 10⁻²</td>
<td>2.9 × 10⁻²[ba]</td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>2.6±0.1 × 10⁻²</td>
<td>2.8±0.1 × 10⁻²</td>
<td>1.4 × 10⁻²[ec]</td>
<td></td>
<td>[51]</td>
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<tr>
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</tr>
<tr>
<td>Brij-98</td>
<td>2.5±0.1 × 10⁻²</td>
<td>2.1±0.1 × 10⁻²</td>
<td>3.0 × 10⁻²[ba]</td>
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<td>[53]</td>
</tr>
<tr>
<td>SS - 1</td>
<td>4.2±0.2 × 10⁻²</td>
<td>3.8±0.2 × 10⁻²</td>
<td>4.2 × 10⁻²[ba]</td>
<td></td>
<td>[54]</td>
</tr>
<tr>
<td>SS - 2</td>
<td>1.1±0.1 × 10⁻²</td>
<td>1.3±0.1 × 10⁻²</td>
<td>2.5 × 10⁻²[ba]</td>
<td></td>
<td>[55] @25 °C</td>
</tr>
</tbody>
</table>

Figure 1
Figure 2

![Graph showing the decay of g²(r) with time in water and 25mM C₄PyCl](image)

- Red circle: P123 in water
- Blue triangle: P123 in 25mM C₄PyCl
Figure 3

Above CMC

Pure 15mM C₄PyCl

δ (ppm)
Figure 4
The cooperative self assembly of Ionic liquid (C₄PyCl) and surfactants/block copolymers acts as tracer for the CMC determination of non-ionic surfactants by conductometry. The proposed method is validated for surfactants with various types of hydrophobic domain with PEO as hydrophilic moiety.