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TBP Induced Double Cloud Point in Aqueous EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13} Solutions: Investigating the Evolution of Associated Micellar Characteristics as a Function of Temperature

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Abstract

Pluronics are considered as potential materials for the removal of tributyl phosphate (TBP) from nuclear fuel reprocessing plants. Recent studies showed that solubilization of TBP in aqueous solution of Pluronic L64 reduces its cloud point (CP) and in addition, induces a second CP at low temperature. In this manuscript we have attempted to understand the origin of this lower CP (LCP) by carrying out DLS, SANS, viscosity and fluorescence measurement studies on 10 % aqueous L64 solutions containing 60 mM TBP. The studies show that on approaching both LCP (≈25°C) and the conventional or upper CP (UCP≈42.5°C), the copolymer solution exhibit a large increase in light scattering intensity and apparent micellar radius. Detailed studies suggest that whereas the copolymer micelles undergo a progressive growth on heating to UCP, they form micellar cluster upon cooling down to LCP due to the onset of inter-micellar attractive interaction. Although such clusters are known to form in micellar solutions of non ionic surfactants on approaching UCP, its formation upon cooling is first of its kind in them. The observed unusual behavior have possibly been triggered by dehydration of micellar corona caused by relocation of TBP from micellar core to corona upon cooling down to LCP.
Introduction

The polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) based nonionic surfactants called Pluronics®, have been subjected to extensive studies for the last few decades because of their rich structural polymorphism and a number of industrial applications. Unlike conventional ionic and nonionic surfactants these triblock copolymers exhibit a strong temperature dependence of their surface active properties in the aqueous medium. At low temperature both the PEO and PPO blocks remains soluble in water and the copolymers exist as unimers. At their characteristic temperature called critical micellar temperature (CMT), they start forming micelles comprising hydrophobic PPO blocks as core and hydrated PEO blocks as corona (shell). With further increase in temperature, the PEO group too becomes insoluble at the cloud point (CP) and they phase separate from the aqueous medium.

Pluronics are good solubilizing agent for poorly water soluble substances, due to which they are considered as suitable for applications in the fields like drug delivery, oil extraction etc. Literature reports show that incorporation of such poorly soluble substances into the Pluronic® micelles leads to micellar dehydration and subsequent observations of sphere-to-rod micellar growth or onset of inter micellar attractive interaction. Recent studies show that aqueous solutions of pluronic P123, P84, L44 and L64 can solubilize tributyl phosphate (TBP) and thus could be considered as potential material for removal of TBP from nuclear fuel reprocessing plants. It has also been shown that its solubilization in these systems leads to a decrease in their CP and in addition induction of a second CP at low temperature, called solubilization minimum temperature (SMT).

Existence of double cloud point is known to occur in aqueous solutions of Pluronic L62 and L92 and some poly-oxyethylene surfactants. It was suggested that in the case of pluronics, the presence of hydrophobic impurity could play a role in inducing the second or lower cloud point. On the
other hand, in the case of TBP solubilized aqueous pluronic systems it has been proposed that the induced second cloud point (SMT) arises due to separation of TBP from the micellar phase.\textsuperscript{27-30} The evolution of the properties of Pluronic L64 micelles on approaching SMT vis-à-vis that observed in the case of normal or upper cloud point is, however, not reported yet. Substances extracted by pluronic micellar solutions can be separated by cloud point extraction method.\textsuperscript{20,34-36} Understanding the fundamental of the existence of the second cloud point in aqueous pluronic solution could thus be of special interest. In view of this we have studied the evolution of the micellar characteristics in TBP solubilized aqueous L64 solution on approaching both SMT and the upper cloud point (UCP). The studies show that whereas the copolymer micelles undergo a progressive growth on heating up to UCP, they form micellar cluster upon cooling down to SMT due to the onset of inter-micellar attractive interaction. Observation of such onset of inter-micellar attraction upon cooling is first of its kind in aqueous micellar solutions of pluronics and non ionic surfactants.

**Experimental**

**Materials and Sample Preparation:**

The triblock copolymer EO\textsubscript{13}PO\textsubscript{30}EO\textsubscript{13} (Pluronic L64) was procured from Aldrich. TBP was obtained from heavy water board, Mumbai, India. Pyrene was obtained from Baker Chemical Co., USA and was re-crystallized twice before use. The copolymer solutions were prepared by weighing required amounts of water, copolymer and keeping them in refrigerator overnight in tightly closed glass vials. Solubilizations of desired amounts of TBP in the copolymer solutions were carried out at room temperature.

**Methods:**
Dynamic Light Scattering (DLS):

DLS measurements were performed using a Malvern 4800 Autosizer employing 7132 digital correlator. The light source was He-Ne laser operated at 633 nm with a maximum power output of 15 mW. Measurements were carried out at five different angles ranging from 50° to 130°. The electric field autocorrelation function vs. time data obtained were analyzed by using method of CONTIN. Analyses at different angles show that the copolymer micelles are diffusive in nature.

Viscometry:

The viscosities of the solutions as a function of temperature were measured in a temperature controlled water bath by using size 50 calibrated Cannon Ubbelohde viscometer with viscometer constant of 0.004065 centi-stokes/sec. The measured flow times of the solutions in seconds were multiplied by the viscometer constant to get the kinematic viscosity of the solutions in centi-stokes. The spread in the flow time remained within ±5 seconds. These kinematic viscosities were then multiplied by the density of water (taken as 1 g/cm³) to obtain the viscosity of the solutions in centi-poise. The relative viscosities of the solutions were then calculated by dividing the obtained viscosity values by the viscosity of water at respective temperatures.

Small Angle Neutron Scattering (SANS):

Experiments: SANS measurements were carried out on the samples prepared in D₂O at the SANS facility at DHRUVA reactor, Bhabha Atomic Research Centre, Mumbai, India. In neutron scattering experiments D₂O is preferred over H₂O for hydrogenous samples for higher contrast. The mean incident wavelength was 5.2 Å with ∆λ/λ = 15%. The scattering data were measured in the wave vector transfer (q= 4πsin(θ/2)/λ, where θ is scattering angle) range of 0.017 to 0.35 Å⁻¹. Samples were held in
HELLMA quartz cells. The measured SANS data were corrected for the background, empty cell contributions and the transmission, and normalized to absolute cross-sectional unit using standard protocols.

SANS Analysis

In SANS, one measures differential scattering cross-section per unit volume \( \frac{d\Sigma}{d\Omega} \) of monodisperse micelles, written as:

\[
\frac{d\Sigma}{d\Omega}(Q) = nV^2 \left( \rho_p - \rho_s \right)^2 P(Q)S(Q) + B
\]

where \( n \) is the number density of the micelles and \( V \) is particle volume. \( \rho_p \) and \( \rho_s \) are scattering length densities of particles and solvent, respectively. \( P(Q) \) is the form factor, characteristic of specific size and shape of the scatterers and \( S(Q) \) is the structure factor that accounts for the inter-particle interaction. \( B \) is a constant term that represents the incoherent background scattering mainly from the hydrogen atoms present in the sample.\(^{38-41} \)

The form factor for micelles consisting of prolate ellipsoidal core of semi major and semi minor axes \( a \) and \( b \) respectively can be given by

\[
P(Q) = \int_0^1 \left[ F(Q, \mu) \right]^2 d\mu \quad (2)
\]

\[
F(Q, \mu) = \frac{3(sin x - x cos x)}{x^3} \quad \text{and} \quad x = Q[ a^2 \mu^2 + b^2(1-\mu^2)]^{1/2}
\]

where the variable \( \mu \) is the cosine of the angle between the directions of \( a \) and \( Q \).

Pluronic\textsuperscript{®} micelles formed in the aqueous medium can be modeled as consisting of hydrophobic core with Gaussian chains (hydrophilic part) attached to it. In this model, the form factor of the micelles \( P(Q) \) consists of four terms: the self-correlation of the core, the self-correlation of the chains,
the cross term between core and chains, and the cross term between different chains, as described in reference 41.

The inter-particle structure factor $S(Q)$ describes the interaction between the particles present in the system and it is the Fourier transform of the radial distribution function for the mass centers of the particle. For very diluted samples, $S(Q) \sim 1$, but for interacting non-ionic micelles it is usually calculated by the analytical solution of the Ornstein-Zernike equation with the Percus-Yevick approximation, utilizing hard sphere interaction.

For polydispersed systems, $d\Sigma/d\Omega$ in equation (1) is modified as

$$\frac{d\Sigma}{d\Omega}(Q) = \int \frac{d\Sigma}{d\Omega}(Q, R) f(R) dR + B \quad \text{(3)}$$

where $f(R)$ is the size distribution and usually accounted by Schultz distribution as given by

$$f(R) = \left( \frac{Z+1}{R} \right)^{Z+1} R^Z \exp\left[ -\left( \frac{Z+1}{R} \right) R \right] \frac{1}{\Gamma(Z+1)}$$

where $\bar{R}$ and $Z$ are the mean value and width of distribution, respectively. The polydispersity of this distribution is given by $\sigma = \sqrt{\frac{1}{Z+1}}$. For simplification, the integration in equation (4) is carried out over $P(Q)$ whereas $S(Q)$ is calculated for the mean size of the particle. The data have been analyzed by comparing the scattering from different models to the experimental data. Throughout the data analysis corrections were also made for instrumental smearing. The modeled scattering profiles were smeared by the appropriate resolution function to compare with the measured data. The fitted parameters in the analysis were optimized by means of nonlinear least-square fitting program.\textsuperscript{38}

**Steady-State Fluorescence Studies:**
Steady-state fluorescence spectra of pyrene in Pluronic solutions were recorded using a Hitachi (Tokyo, Japan) model F-4500 spectro-fluorimeter. Pyrene has been extensively used as a fluorescence probe to investigate the formation of hydrophobic micro-domains by surfactants and copolymers.\textsuperscript{42} The excitation wavelength was 335 nm and the emission spectra were recorded from 350 to 450 nm. The excitation and the emission band width were 1 nm for both. The scan speed was 60 nm/min and all spectra were averaged over four scans. Initially pyrene stock solution was prepared in methanol. Requisite amount of stock solution was taken in a glass vials and the solvent was evaporated under stirring condition such that a thin coating of pyrene forms inside the glass vial. Appropriate amount of Pluronic solution was added to the glass vial and stirred overnight. The final concentration of pyrene in each solution was $1 \times 10^{-6}$ M. No excimer formation has been observed in the micellar solution.

\textbf{Figure 1:} Light scattering intensity as a function of temperature recorded at 130° scattering angle of 10% L64 solution with and without 60 mM TBP.
Results and Discussion

In order to understand the evolution of the properties of TBP solubilized L64 micelles on approaching the lower and upper cloud points, we carried out DLS studies on 10% L64 solution containing 60 mM TBP as a function of temperature. The plot of light scattering intensity with temperature depicted in Figure 1 shows that like in the case of UCP, scattering intensity undergoes a monotonous increase on approaching LCP. This suggests that the micelles either grow or show onset of inter micellar attractive interaction on cooling the solution temperature down to LCP. Such behavior is absent in pure copolymer solution where an increase in scattering intensity is observed only upon heating to UCP with no existence of LCP (figure 1). Aqueous solutions of pluronics and other non ionic surfactants containing PEO group show such phenomena on approaching UCP due to a progressive increase in hydrophobicity of the surfactant molecules with increase in temperature. In fact due to a decrease in hydrophobicity of the surfactant molecules these systems should show weakening of aggregation characteristics with decrease in temperature. The observed unusual increase in light scattering intensity upon cooling is thus first of its kind in pluronic and other PEO-based non-ionic micellar systems and is expected to result only due to the presence of TBP within the micellar structure.

To shed further light on it we have shown the evolution of the correlation function plot associated with the observed increase in the scattering intensity on approaching the cloud points and the results of their analysis based on CONTIN method in Figure 2. The data recorded at scattering angle of 130° are reported instead of those at 90° since at 130° we have the advantages of getting higher scattering intensity and less interference from possible presence of unwanted scattering objects. Figure 2 shows that at 31.5°C, where lowest intensity is observed, the correlation function plot is single exponential. It remains so upon cooling down to LCP but changes to bi-exponential on approaching UCP. This can be
observed from size distribution plots, which show appearance of second scattering species near upper cloud point. The plots also suggest that apparent micellar size increases on approaching both the cloud points and the amount of apparent growth is higher in the case of LCP.

![Correlation function plots and size distribution plots](image)

**Figure 2:** Correlation function plots recorded at 130° scattering angle and the corresponding size distribution plots obtained by CONTIN method of fitting for 10% L64 solutions with 60 mM TBP. The solid lines with the correlation function plots are fit to the data.

To understand more about the evolution of the micellar characteristics as a function of temperature in this system, we have studied the variation of relative viscosity of the copolymer solution as a function of temperature on approaching the two cloud points. Viscosity of pure aqueous L64 solution increases with increase in temperature up to the cloud point due to a progressive increase in the aspect ratio of the elliptical L64 micelles. Figure 3 shows that TBP solubilized L64 solution too, exhibit similar increase in viscosity on approaching UCP, which supports the observed micellar growth shown.
by DLS studies. This suggests that the observed bi-exponential nature of the correlation function near UCP as shown in figure 2, arise due to micellar entanglement and consequent stress relaxation mechanism as reported to occur in many concentrated rod like micellar systems.$^{46,47}$ Quite interestingly, in spite of the fact that there is larger apparent micellar growth on approaching LCP as compared to that observed in the case of UCP, the associated viscosity enhancement is found to be much less significant. This suggests that the micelles do not grow but undergo cluster formation upon cooling down to LCP due to onset of inter micellar attractive interaction. Similar apparent micellar growth with single exponential correlation function as a result of micellar cluster formation in the presence of inter micellar attractive interaction were earlier reported in different micellar and reverse micellar systems.$^{48-51}$ The viscosity enhancement associated with onset of inter micellar attractive interaction on approaching cloud point are reported to be much smaller$^{52-54}$ than that observed in the case of micellar growth leading to formation of worm like micelles.$^{48}$

![Figure 3: Relative viscosity of 10% L64 solution containing 60 mM TBP as a function of temperature. Inset shows an enlarged view of the viscosity enhancement at low temperature.](image)
Table 1: Fitted parameters obtained from the analysis of the SANS data for 10% L64 solutions containing 55 mM TBP as a function of temperature.

<table>
<thead>
<tr>
<th>Temp</th>
<th>$R_C$(Å)</th>
<th>Aspect Ratio</th>
<th>$N_{agg}$</th>
<th>$R_g$(Å)</th>
<th>Volume Fraction</th>
<th>$R_{HS}$(Å)</th>
<th>P.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>28°C</td>
<td>28.8</td>
<td>3.72</td>
<td>128.2</td>
<td>3.7</td>
<td>0.12</td>
<td>77.7</td>
<td>6.5</td>
</tr>
<tr>
<td>31°C</td>
<td>28.4</td>
<td>4.3</td>
<td>143.5</td>
<td>5.6</td>
<td>0.149</td>
<td>74.0</td>
<td>9.6</td>
</tr>
<tr>
<td>34°C</td>
<td>27.8</td>
<td>4.87</td>
<td>151.3</td>
<td>7.88</td>
<td>0.152</td>
<td>74.2</td>
<td>9.29</td>
</tr>
<tr>
<td>38°C</td>
<td>28.8</td>
<td>6.0</td>
<td>208.4</td>
<td>7.4</td>
<td>0.14</td>
<td>77.8</td>
<td>11.0</td>
</tr>
<tr>
<td>42°C</td>
<td>29.4</td>
<td>6.74</td>
<td>245.4</td>
<td>7.1</td>
<td>0.117</td>
<td>82.4</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Figure 4: SANS patterns of 10% L64 solutions containing 55 mM TBP as a function of temperature. The solid lines represent fit to the data. Inset shows the plots in log-log scale.

To corroborate the results obtained from viscosity data we have carried out SANS measurements on 10% L64 solutions containing 55 mM TBP as a function of temperature, which are shown in figure 4. The solution shows lower and upper CPs of 26°C and 43°C, respectively. TBP molecules are considered to be present in the core as per the NMR studies reported in the literature and therefore,
contribution from them has also been taken into account for SANS data analysis. The analysis of the data reveals that in agreement with the literature,\textsuperscript{43} the micelles of this system are elliptical in nature, the aspect ratio of which increases monotonously with increase in temperature (Table I). The shape of Pluronic L64 micelles has been a debatable issue. Literature report\textsuperscript{54} shows that these micelles form with spherical structure. Our attempt to fit the SANS data based on spherical form factor however, showed unacceptably low values of micellar volume fraction (lower than the volume fraction of the copolymer) and very high values of the normalization constant (between 4-5).\textsuperscript{43} Theoretical study carried out on this system\textsuperscript{55} suggested that L64 micelles prefer a prolate ellipsoidal structure to sphere and our attempt to fit the data based on an ellipsoidal core-corona model also resulted in rational values of the fitted parameters as reported by us earlier.\textsuperscript{43} Though we attempted to study the variation of the micellar structure on approaching LCP (26°C), because of the low temperature limit of the measurement as the room temperature, the measurements could be extended only up to 28°C. On the other hand in the concentration range of TBP where stable micellar structures are formed,\textsuperscript{27} 26°C was the maximum lower cloud point of the copolymer solutions in D\textsubscript{2}O.

As shown in figure 4, while there is systematic change in the shape of the SANS plot from 31°C to 42°C, the plot at 28°C, shows higher scattering intensity at low Q values leading to a shift in the plot to lower Q region. This, along with the observed increase in viscosity of the copolymer solution on approaching LCP (figure 3) with a decrease in aspect ratio of the micelles (Table 1), suggests that intermicellar attraction in this system becomes stronger as temperature approaches its LCP. To confirm the presence of intermicellar attraction at 28°C, we have to analyze the data based on the presence of intermicellar attraction with an elliptical shape of the micelles. We did not attempt to carry out such analysis as it will involve fitting of a very large number parameters, which will be a difficult proposition. Instead we did additional DLS studies on the variation of apparent hydrodynamic radius of the micelles as a function of Pluronic L64 concentration just below the LCP of this system. These SANS data
however, do support the results obtained from DLS and viscosity studies that the variation of the micellar properties are different on approaching the lower and upper cloud points.

![Diagram](image)

**Figure 5:** The variation of average micellar hydrodynamic radius obtained at 130° scattering angle from CONTIN method of fitting as a function of Pluronic L64 concentration in the presence of TBP.

Figure 5 shows that in the presence of TBP, the apparent micellar size increases with increase in Pluronic L64 concentration at temperatures just below the respective LCPs. Solubility of TBP in L64 micellar solution increases with increase in L64 concentrations. The TBP concentrations taken corresponding to L64 concentrations of 3%, 5%, 7%, 10% and 12% were 15 mM, 30 mM, 45 mM, 60 mM and 75 mM, respectively. To ensure the presence of attractive inter micellar interaction, the measurements were carried out at 0.5°C above the respective lower cloud points. The reason for this is that in systems containing inter micellar attractive interaction, the properties of the micelles at any temperature is determined by its difference with the cloud point of the micellar solutions. The observed increase in the hydrodynamic radius with L64 concentrations in figure 5 is similar to those
reported in micellar\textsuperscript{56} and reverse micellar systems\textsuperscript{51,57,58} with attractive inter micellar attractions. This suggests that an attractive inter micellar interaction exists in this system near LCP. Absence of large increase in viscosity of the copolymer solution in the presence of attractive inter micellar interaction was explained by Corti and Degiorgio\textsuperscript{44} and Zulauf and Rosenbusch\textsuperscript{45} based on the formation of large but loosely bound statistical clusters. These clusters include both micelles and water and are formed when micelles are correlated over a distance much larger than the size of the micelles.\textsuperscript{44,45} It has been argued that weak nature of attractive interaction is responsible for such behavior, as a strong micellar attraction interaction would result in large increase in viscosity due to the formation of stable and compact cluster.

![Figure 6](image.png)

**Figure 6:** $I_1/I_3$ peak ratio of pyrene fluorescence spectra as a function of temperature.

To discuss about the possible reason for the observed LCP in the present system, pure Pluronic L64 micellar solution does not show this CP, so the presence of TBP in micellar structure must be responsible for inducing it. Literature reports suggest that TBP being sparingly soluble in water prefers to stay in the micellar core.\textsuperscript{30} To verify this we have carried out pyrene fluorescence studies on this
system in the presence and absence of TBP as a function of temperature (figure 6). The intensity ratio of the first (374 nm) and the third (385 nm) vibronic band of pyrene, commonly termed as $I_1/I_3$, decreases with the increase in hydrophobicity of its surrounding environments. Pyrene thus has been used to study the micro-domain of different class of micro-heterogeneous media, including Pluronic micelles.\textsuperscript{59} In the case of pluronics, it is well understood that because of non-polar character of pyrene, it resides in the micellar core and any alteration in the $I_1/I_3$ peak ratio is basically an indication of alteration in the hydration behavior of the core. Figure 6 shows that in the temperature range studied, solubilization of TBP leads to a decrease in $I_1/I_3$ ratio, which suggests that hydrophobicity of the micellar core increases in the presence of TBP. This agrees with the report suggesting that TBP molecules preferably occupies core of the L64 micelles.\textsuperscript{30} Both in the presence and absence of TBP, the $I_1/I_3$ ratio of the pyrene fluorescence spectra increases with decrease in temperature due to a progressive decrease in hydrophobicity of the micellar core.

Regarding the origin of onset of inter micellar attraction on approaching LCP in the TBP solubilized L64 solution, it is quite possible that as the core becomes increasingly hydrophilic with decrease in temperature, the preference of TBP for it could decrease and part of it could get relocated to micellar corona. TBP has about 16 mM solubility in water at room temperature\textsuperscript{27} so there is always a possibility of its partitioning between core, corona and even bulk water. The relocation of TBP to micellar corona may lead to its dehydration and consequently induce inter micellar attraction. A decrease in micellar volume fraction obtained from SANS studies as the temperature decreases from 31°C to 28°C (table 1), could be linked to dehydration of micellar corona on approaching LCP. In literature it has been suggested that dehydration of micellar corona with increase in temperature induces micellar adhesion due to interpenetration of polymer chains and consequent depletion of the solvent in the corona region when two micelles come into contact.\textsuperscript{60} A few reports also show that poorly water soluble substances like Parabens\textsuperscript{26} and Salicylic Acid\textsuperscript{61} occupy corona region of pluronic
micelles and brings about micellar dehydration and subsequent sphere-to-rod micellar growth or micellar attraction driven cluster formation.

**Conclusion:**

In conclusion, in this manuscript we have investigated the evolution of micellar properties in TBP solubilized aqueous Pluronic L64 solutions as a function of temperature up to the phase boundaries by DLS, SANS, viscosity and fluorescent measurement techniques. Beside the conventional or upper cloud point (UCP), these systems also show a lower cloud point (LCP), which has been explained in literature as solubilization minimum temperature (SMT) of TBP in the micellar system. Our studies show that like in the case of UCP, the aggregation characteristics of the copolymer solution undergo systematic changes on approaching LCP, leading to an observation of a monotonous increase in light scattering intensity and apparent micellar radius with decrease in temperature. Detailed studies however, suggest that whereas the copolymer micelles undergo a progressive growth on heating to UCP, they form micellar cluster upon cooling down to LCP due to the onset of inter-micellar attractive interaction. Such cluster formations are known to occur in micellar solutions of non ionic surfactants on approaching UCP due to a progressive increase in the hydrophobicity of the surfactant molecules with increase in temperature. Its occurrence upon cooling, however, is first of its kind in these systems. The obtained insight into the observed solubilizate driven phase separation in aqueous pluronic system at low temperature finds importance because of their possible application for cloud point extraction method.
References:


TBP solubilized Pluronic L64 solutions exhibit inter-micellar attraction driven micellar cluster formation upon cooling, which is unique in non-ionic micellar systems.