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ORIGINAL CONTRIBUTION

Urea-induced demicellization of Pluronic L64 in water

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Abstract The micellar behavior of a polyethylene oxide block–polypropylene oxide block–polyethylene oxide copolymer Pluronic L64 in aqueous urea solutions (urea concentrations 0, 1, 2, 3, 4, and 6 M) by physical methods, viz. cloud point and viscosity, spectral techniques (Fourier transform infrared, fluorescence, and nuclear magnetic resonance), differential scanning calorimetry, and dynamic light scattering is reported. The presence of urea causes an increase in the clouding temperature, critical micellization temperature, and the structural transition (spherical micelles to ellipsoid/rod) temperature; different methods showed good agreement. Urea induces demicellization of L64, enhancing accumulation of water molecules surrounding micelles. L64 micelles show growth at high temperatures, but this micellar transition is suppressed by urea, as proven by calorimetric and viscometric methods. The results are discussed in terms of the molecular mechanism underlying the effects of urea.

Keywords Demicellization · Critical micellization temperature (CMT) · Aggregation number

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Introduction

Hydrophobic interactions are primarily responsible for micellization of surfactants and tertiary structure of proteins in aqueous solutions. In fact, clouding and aggregation behaviors of surfactants and the protein denaturation are closely related phenomena. However, the effect of urea on proteins or supramolecular aggregates such as micelles is yet a debated issue. It is known that the presence of urea (known as protein denaturant) shifts micelle formation and micellar transitions to higher concentrations, decreases counter ion binding in ionic micelles, and hence decreases aggregation number. The effect of urea has been found to raise the critical micelle concentration (CMC) [1, 2], but a decrease in CMC at low urea concentrations was also evident [3–5].

polyethylene oxide block–polypropylene oxide block–polyethylene oxide (PEO–PPO–PEO) triblock copolymers, known as Pluronics, are commercially available in a variety of molecular weights and PEO/PPO ratios [6]. These copolymers form micelles with the hydrophobic core consisting of PPO blocks and an outer shell of the hydrated PEO above CMC in water and salt solutions [7–12]. The formation of triblock copolymer micelles is temperature-dependent, resulting in a dramatic decrease of the CMC upon a small increase in temperature. This arises because the temperature induced dehydration of the constituting blocks. The hydrophobic/hydrophilic character of the copolymer in aqueous solution can be altered by varying the solution temperature or modifying the properties of aqueous solvent. As a result, amphiphilic copolymers have found widespread applications in emulsification, solubilization and controlled release, as well as product formulation in industries ranging from agriculture to pharmaceuticals [9, 13–15].

Two different mechanisms have been proposed to explain the action of urea in aqueous solutions: (1) an indirect mechanism, according to which urea acts as a “structure breaker” and thus facilitates the hydration of non-polar solutes [16, 17] and (2) a direct mechanism, consistent with urea has almost no effect on the water structure, replaces some of the water molecules in the hydration shell of the solute, and self-associates [18]. However, a fundamental understanding of these effects remains a challenging unsolved problem. Addition of urea increased the CMC of nonionic [2, 19] and ionic surfactants [20], decreased the hydrodynamic radius of nonionic [19] and ionic micelles [21], and raised the cloud point temperatures of nonionic surfactant solution [19, 22].

We noticed through literature that a great deal of research work is already completed to understand effect of various additives, e.g., electrolytes, alcohols, hydrotropes, etc. on Pluronic solutions [16–21]. Though a complete study describing an effect of urea on triblock copolymer is still lacking to the best of our knowledge, in this paper, the effect of urea on a triblock copolymer L64 ($EO_{13}PO_{30}EO_{13}$, total molecular weight 2,900, % PEO 40) has been studied by various techniques, viz. cloud point, viscosity, fluorescence, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), dynamic light scattering (DLS), and differential scanning calorimetry (DSC) measurements. Solution (2%) of nonionic surfactant L64 exists as micelles at 30 °C with hydrodynamic diameter of about 18 nm. Our aim was to examine how these micelles disintegrate in the presence of urea. The demicellization of any nonionic surfactant in the presence of any additive has been tried before. An attempt is made to understand molecular mechanism underlying urea-induced L64 demicellization making use of some analytical techniques.

Materials and methods

Pluronics L64 was obtained from BASF, Mount Olive, NJ, USA and used as received. Analytical grade (BDH, England) urea was used. Fresh solutions of L64 (2 wt.% unless stated otherwise) at different urea concentrations in double distilled water were used. For DLS measurement, Milli-Q water having specific resistance 18.2 MΩ cm and for NMR experiments D_2O was used.

Cloud point

Cloud point measurement is an effective study to understand the phase separation and structural transition in block copolymer systems. For PEO–PPO–PEO block copolymers, the dehydration of polyethylene oxide moiety at higher temperature results in a complete phase separation, known as the cloud point. The clouding phenomenon shows that the interactions between the PEO chains become increasingly attractive with increasing temperature in aqueous solution or, in other words, water becomes a less good solvent.

Measurements were carried out at fixed concentrations of the copolymer (1–10 wt.%) in the absence and presence of various amount of added urea by gently heating solution in thin 20-ml glass tubes immersed in a water bath well stirred with a magnetic bar while being heated. The heating rate was controlled to 1 °C/min. The first appearance of turbidity was taken as the cloud point. The cloud point of copolymer in water agrees with that reported in the literature [23], and the cloud point (CP) values were reproducible up to 0.5 °C.

Viscosity measurement

Viscometry has been used extensively to provide information on the hydrodynamic properties of Pluronic solutions. Flow time is measured for the solvent and the copolymer solution using a capillary viscometer. The ratio of the flow time of solution to that of the solvent is taken as the relative viscosity for the copolymer solution. The drastic increase in the relative viscosity of Pluronic block copolymer reveals the possibility of phase transition. A sudden rise in the viscosity for a polymer is indicative of sphere-to-rod transition [24, 25].

The viscosity measurements were carried out using an Ubbelhode suspended level capillary viscometer [26]. The viscometer was always suspended vertically in a thermostat with a temperature stability of ±0.1 °C in the investigated region. The viscometer was cleaned and dried every time before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch.

Differential scanning calorimetry

A conventional DSC involves measuring the differential power necessary to maintain a given temperature for two pans containing the polymer and the reference sample. In DSC, the phase transition is indicated by sharp endotherm or exotherm which causes change in the differential power supplied to the sample. The technique provides the enthalpy of the micellization, CMC, and the critical micellization temperature (CMT). The micellar transition temperature can also be calculated. The technique is discussed in detail elsewhere [27].

DSC measurements were performed with a Microcal MC-2 instrument (Microcal, Amherst, MA, USA). The MC-2 high sensitivity scanning calorimeter contains a fixed pair of matched tantalum cells (cell volume ~1.2 ml) which are filled with the sample and the reference solution, respectively. The solutions of copolymer samples, with and without urea, were prepared at room temperature using doubly distilled deionized water. The sample solution was then injected into the sample cell and the reference cell filled with water. A nitrogen cylinder is normally set at one atmosphere-maintained pressure in the cells to suppress the formation of air bubbles during scanning. Temperature scans were performed at a rate of 1 °C/min and in the range of 10–90 °C. All samples show three endothermic transition peaks on heating. The baseline was drawn with the help of ORIGIN software supplied by Micro cal Inc. The points before and after a thermal transition were selected manually (and set to zero), and a baseline was fitted to pass through these points.

Dynamic light scattering

Dynamic light scattering measurement generates particle–particle correlation decay as a function of time (in microsecond) from scattered intensity fluctuation, which is called the normalized autocorrelation function of the light intensity, $g^{(2)}(t)$, which is related to the electric field normalized correlation function, $g^{(1)}(t)$, through the Siegert relation [28]:

$$g^{(2)}(t) = 1 + \beta \left| g^{(1)}(t) \right|^2 \tag{1}$$

where β is the coherence factor ($0<\beta\leq1$), $g^{(1)}(t)$ can be written as the Laplace transform of the distribution of the relaxation rates, $G(\Gamma)$:

$$g^{(1)}(t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\,\mathrm{d}t \tag{2}$$

where Γ is the relaxation rate and the diffusion coefficient,

$$D = \Gamma / Q^2. \tag{3}$$

The micellar hydrodynamic diameter (d_h) was obtained using the Stokes–Einstein equation:

$$D = \frac{k_B T}{3\pi\eta d_\mathrm{h}}. \tag{4}$$

DLS measurements were performed using a Malvern 4800 Autosizer employing 7132 digital correlator. The light source was argon ion laser operated at 514.5 nm with a maximum output power of 2 W. The average decay rate (Γ) of the electric field autocorrelation function, $g^1(\tau)$, was estimated using the method of cumulants. The apparent diffusion coefficients (D) of the micelles were obtained from the relation $\Gamma = Dq^2$ (q is the magnitude of the scattering vector given by $q=[4\pi n \mathrm{Sin}(\theta/2)]/\lambda$, n being the refractive index of the solvent, λ, the wavelength of laser light, and θ is the scattering angle), and the corresponding apparent hydrodynamic diameters (D_h) were calculated using the Stokes–Einstein relationship. For all the solutions, Γ varies linearly with 'q^2,' indicating translational diffusion of the scatterers.

Fluorescence spectroscopy

This method relies on changes in the fluorescence of the free probe molecules or probe tagged to copolymer chain. For the commonly used probe pyrene, the intensity of the first and the third vibronic peak changes depending on the local polarity. Pyrene is used due to its low solubility in water, long fluorescence lifetime, and sensitivity to the polarity of its environment. The technique provides the CMT for copolymer system by intersection of the two lines in the spectra, as will be discussed later. An excellent review provides more detailed information on all aspects of fluorescence experiments on block copolymer solution [29].

The micropolarity in copolymer solutions in urea/water was probed as a function of temperature using the I_1/I_3 intensity ratio of the pyrene vibronic fine structure in fluorescence emission spectra. The fluorescence emission spectra of excited state monomeric pyrene solubilized in the investigated solutions were recorded with a Jasco FP-6500 spectrofluorometer in the range 350–500 nm using an excitation wavelength of 330 nm. The fluorescence intensity ratio of the first and third vibronic bands (I_1/I_3) was used as a spectroscopic tool to qualitatively measure the polarity of the probe microenvironment in micelles/unimers.

Fourier transform infrared

Infrared spectroscopy gives information on molecular vibrations or more precisely on transitions between vibrational and rotational energy levels in the molecule. The spectrum is obtained when the frequency of the molecular vibrations corresponds to the frequency of the infrared radiation absorbed. The stretching vibrations in the PPO and PEO blocks of the copolymer can be monitored using this technique. The plot of wavenumber vs. temperature can provide CMT for a copolymer solution, as will be discussed later.

The FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm^{-1} using a deuteriotriglycine sulfate detector. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. This system comprised a Graseby–Specac temperature cell (P/N 21525), and the temperature measurement is accurate to 0.1 °C. The equilibration time for each measurement was 1 min. FTIR spectra of all samples were recorded using a BaF_2 cell from 5 °C to 60 °C by scanning 64 times. The OPUS spectroscopic software was used for the data handling.

Nuclear magnetic resonance

NMR has been widely used to probe micelle structure. Proton NMR on copolymer solution in D_2O is employed to monitor the presence or absence of micellization. NMR provides distinct evidence about the micellar changes in the Pluronic solution based on the changes in the local environment of the PO –CH_2 and the PO –CH_3 groups. The change in chemical shift and line shape of the PO –CH_3 protons will provide the molecular evidence of aggregation or de-aggregation of Pluronic polymer in water. This technique is also used for calculating the CMT for block copolymer solution. Wanka et al. [30] have used this technique to locate the critical micellization temperature where the fine structure associated with PO units present for molecularly dissolved unimers disappear above the CMT.

All NMR experiments were conducted on a Bruker Avance 600 spectrometer at Larmor frequency of 600.13 MHz for proton, equipped with a microprocessor-controlled gradient unit and an inverse-detection multinuclear BBI probe with an actively shielded z-gradient coil. The sample temperature was kept constant within ±0.1 °C by the use of a Bruker BCU-05 temperature control unit. For all experiments, the samples were allowed to equilibrate at the desired temperature for at least 15 min prior to measurement; experiments that were repeated at the same temperature, but reached by a temperature change in the opposite direction, yielded identical results. Chemical shifts (δ) are relative to internal DSS standard (δ=0.000 ppm in ^{1}H NMR spectra for all temperatures and concentrations according to the IUPAC recommendations).

Results and discussion

The clouding behavior of nonionic surfactants in water is an interesting feature involving their practical usefulness. The CP of nonionic surfactant can be conveniently decreased or increased by adding various additives. Cloud points of copolymer L64 (1%, 2%, 5%, and 10%) in urea solutions (0–6 M) are shown in Fig. 1. The CP values for copolymer in the absence of urea agree well with the reported values [23]. The clouding phenomenon of PEO-based nonionic surfactants has been much debated, and different interpretations based on the conventional dehydration of PEO moiety, hydrogen bonding between ethereal oxygen of PEO and water molecules, and polar/non-polar conformations of PEO are provided. Addition of urea to L64 solutions increases the CP, which can be interpreted in terms of the interaction between the ethylene oxide head groups and the water [31]. The addition of urea will increase the dielectric constant of water and thus results in greater van der Waals interaction at a constant temperature [32], which will enhance the hydration of the EO segments and cause higher cloud point values.

The relative viscosity of 2% L64 in water and in the presence of urea (0–6 M) as a function of temperature was measured and presented in Fig. 2. According to the direct mechanism proposed earlier by Alexandridis et al. [2], urea would affect the micellization process by replacing some water molecules and self-associating in the micellar system without affecting the water structure. It is observed that the onset temperature corresponding to the sharp increase in relative viscosity increases with increasing urea concentration. It can be clearly seen that the viscosity of copolymer solution experiences a sudden rise at a certain temperature. This elevation in the viscosity may be the cause of sphere to rod transitions in L64 solution. On addition of urea, this onset of transition shifts to higher temperature and almost diminished at very high concentration of urea (6 M) in the temperature range 20–70 °C. The viscosity then remains almost constant even at 70 °C. With increase in urea concentration, the onset of the sudden rise in relative viscosity curve shifts to higher temperature side. The onset temperature for this micellar transition increases in the order of 0>1>2>3>4>6 M. The increase in onset temperature could be attributed to the hydration of PEO moiety with increasing urea concentration, leading to more elongated structure. In other words, urea plays a non-cooperative role in micellization, causes the demicellization and reduces the aggregation number [19, 21]. Earlier reports by Kumar et al. [33] presented similar observations on interaction of urea family with surfactant micellar system.

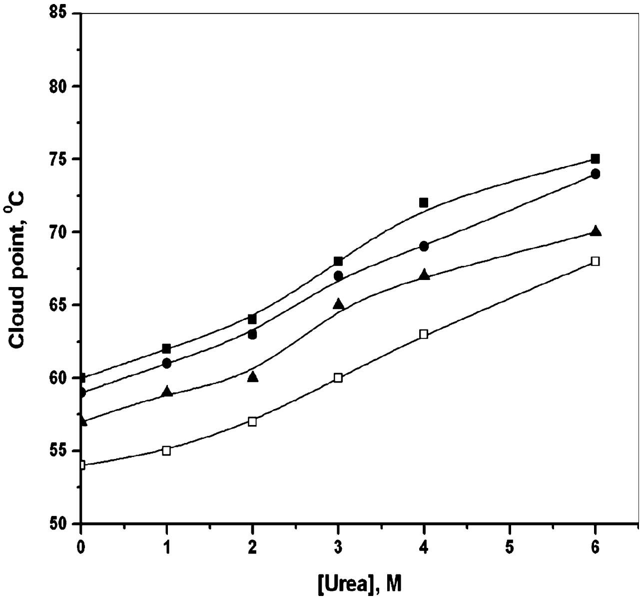


Fig. 1 Cloud point of L64 as a function of urea concentration. (*filled square*) 1%, (*circle*) 2%, (ttriangle) 5%, (*open square*) 10%

DSC technique is found to be a good tool in determining the CMT of Pluronic solutions. The presence of endothermic peaks associated with the micelles formation and clouding in the DSC scans were previously reported for several Pluronics [34, 35]. DSC curves for Pluronic L64 (2%) in presence of different concentrations of urea (0–4 M) were shown in Fig. 3. In addition to the main endothermal peak

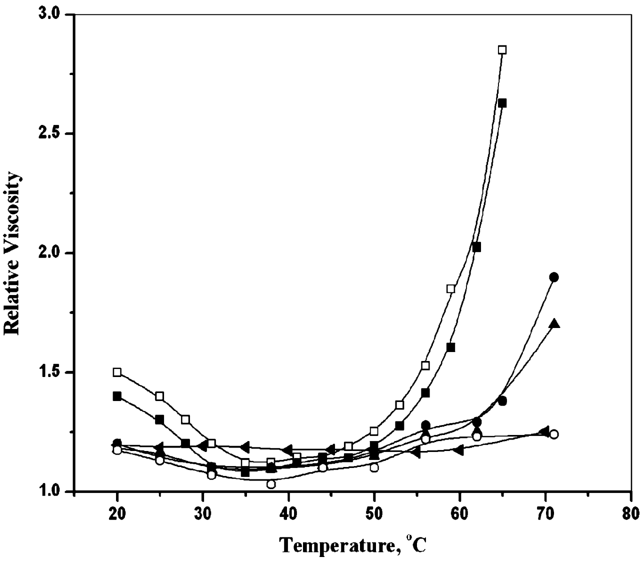


Fig. 2 Relative viscosity of 2% L64 as a function of temperature in presence of urea. (*open square*) 0 M, (*filled square*) 1 M, (*circle*) 2 M, (*triangle*) 3 M, (○) 4 M, (*left triangle*) 6 M

associated to the micellization, the other peak at higher temperature is associated to the clouding of solution. Another small peak indicated in the figure as transition region may be attributed to the presence of bigger micelles, perhaps due to change in the shape of spherical micelles to ellipsoid/rod. The low-temperature micellar transition is large, endothermic, and broad. The broadness is due to the temperature dependence of the amount of unimers in equilibrium with the micelles. The large endothermic nature of the micellization enthalpy and the negative free energy (because of the spontaneous temperature induced micellization) suggest the positive entropy contribution in micelle formation, which actually originates from the entropy gain by water when the copolymers associated and also from the decrease in the polarity of EO and PO segments as temperature increases. In this figure, all peaks, including the peak representing precipitation, shifted to higher temperatures when the urea concentration was increased. The onset of these transitions is denoted in Fig. 3. Here, the lower temperature peak has the largest amplitude and corresponds to the formation of micelles. The explanations for the change of CMT or CP by varying urea concentration are already given as salting-in effect, and hence, demicellization occurs. It can be observed that the value of CMT rises to 38.8 °C from initial (in absence of urea) value of 33.5 °C on addition of 4 M urea to 2% L64 solution. According to earlier report [2] based on thermodynamic study on block copolymer, it was concluded that hydrophobic interaction increases entropy of the system. On addition of urea, the amplitude of enthalpy changes, but it does not affect the mechanism of micellar aggregation which is stated to be entropy-driven. DSC shows the precipitation at higher temperature; some workers considered it as CP, but it is the complete phase separation region [36]. The sphere-to-rod micellar transition temperature (MTR) obtained from DSC shows that addition of urea retards the sphere-to-rod transition and moves rod formation to higher temperatures. The CMTs and MTR are reported in Table 1.

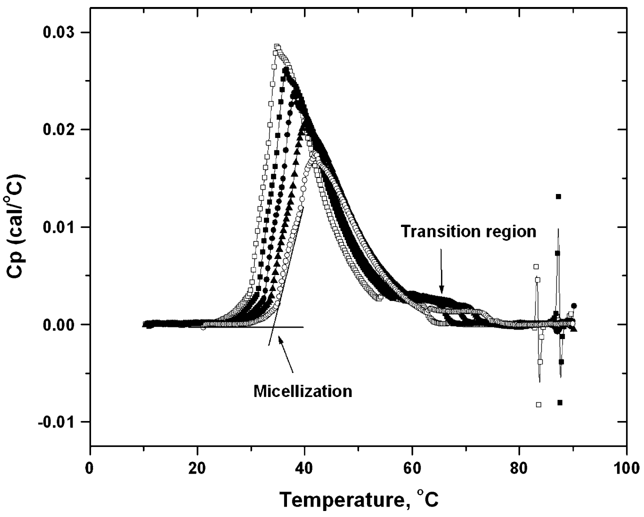


Fig. 3 DSC thermograms for 2% L64 in the absence and presence of urea at different concentrations: After base line correction. (*open square*) 0 M, (*filled square*) 1 M, (*filled circle*) 2 M, (*triangle*) 3 M, (*open circle*) 4 M

IR spectroscopy can be taken as signature to obtain information on change in the micellar behavior of Pluronic. The position of the C–O–C stretching band in the IR spectrum of block copolymers is sensitive to the aggregation process. Thus, the changes in the wavenumbers of C–O–C stretching band of PEO chains can be used as an indication of micelle formation/deformation in copolymer solution. Earlier studies [37–38] have used this technique to monitor the conformation of hydrocarbon chains in the normal low-molecular-weight surfactant micelles in aqueous solutions, which can be accordingly employed for Pluronic block copolymers. The FTIR scans for the 2% L64 in different urea concentrations (0–4 M) at different temperatures were measured,

Table 1 CMTs (°C) for 2% L64 in different urea concentrations obtained from fluorescence, IR spectroscopy, and DSC

Urea (M)	Fluorescence	FTIR	DSC	MTR[a] (°C)
0	32.5	32.5	33.5	55
0.5	33.0	–	–	–
1	33.5	33.0	35.0	56
2	35.0	36.0	37.5	57
3	36.5	38.0	38.0	59
4	38.5	40.0	38.8	61
6	41.0	–	–	–

[a] Sphere-to-rod transition temperatures obtained using DSC

and the wavenumber of C–O–C stretching vibration bands were presented in the Fig. 4.

The wavenumber of C–O–C stretching vibration bands moves towards higher values with increasing temperature, indicating that the dehydration of PPO block occurred as the temperature elevates. As a result, the C–O–C region of the PPO moiety will experience a hydrophobic microenvironment [25]. The CMT of aqueous solutions of 2% L64 in the presence of various concentrations of urea increased with increasing urea concentration. The obtained CMT values were found to increase in the order $H_2O<1<2<3<4$ M. On addition of 4 M urea to the L64 solution, the CMT showed considerable increase to settle at 40 °C from initial 32.5 °C. The shift in the CMT value was successfully correlated with change in CP of copolymer solution. A common mechanism involving weakening of hydrophobic interaction by urea causing the demicellization of block copolymer may exist.

The NMR spectroscopy can provide useful information on the change in the micellar environment of the block copolymer. To investigate the demicellization induced by urea, the H^1 NMR spectra for 2% L64 in water in the absence and presence of urea were measured at various temperatures. The local expanded regions of the PO $-CH_2-$ and the PO $-CH_3$ signals with increasing urea concentration and temperatures were presented in Fig. 5a,b, respectively. Here, the broad peaks from 3.45 to 3.65 ppm belong to the PO $-CH_2-$ groups. Distinct signals were obtained here in the absence of urea at lower temperatures in Fig. 5b. It is clear that the hyperfine structure of the PO $-CH_2-$ signals and the triplet of the PO $-CH_3$ signal disappear and both the PO $-CH_2-$ and $-CH_3$ signals broaden at higher temperature. An increase in temperature will drive the chemical shift of the PO $-CH_3$ protons towards lower ppm values. The change in the line shape of the PO group is the result of conformational change in the PPO chain [39], whereas the broadening of the peaks indicates the reduction in the mobility of the PPO segments [40]. Here, with the addition of urea, chemical shift exhibits large downfield

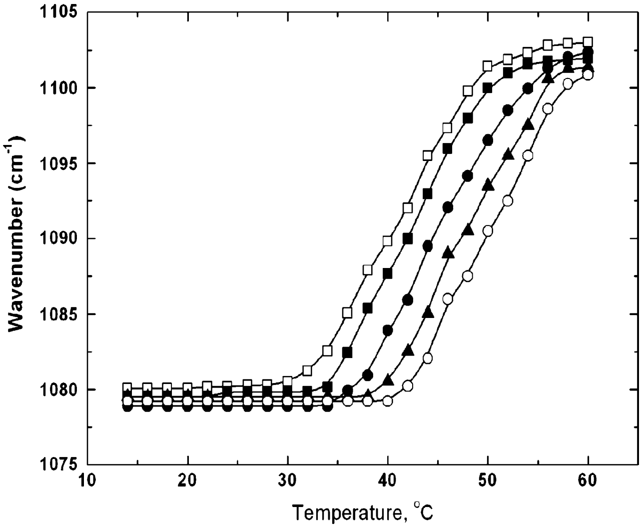
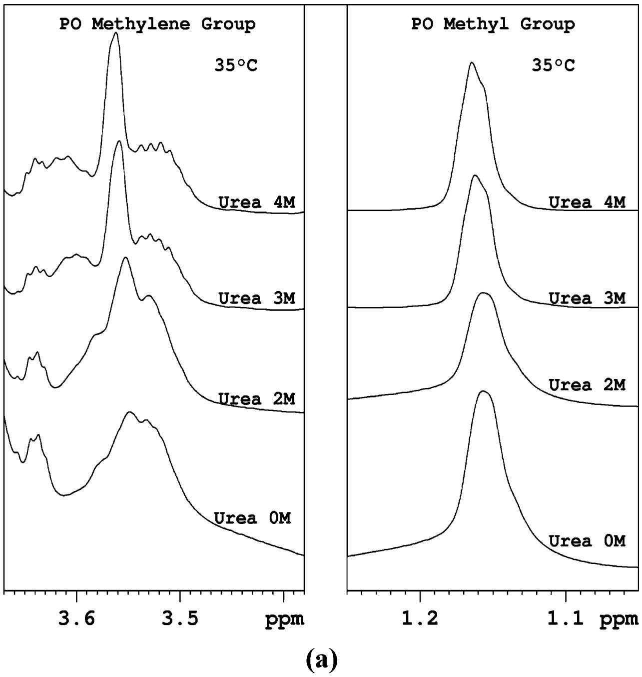


Fig. 4 Wave-number shift of the C–O–C stretching vibration band of 2% L64 in water vs. temperature. (*open square*) 0 M, (*filled square*) 1 M, (*filled circle*) 2 M, (*triangle*) 3 M, (*open circle*) 4 M



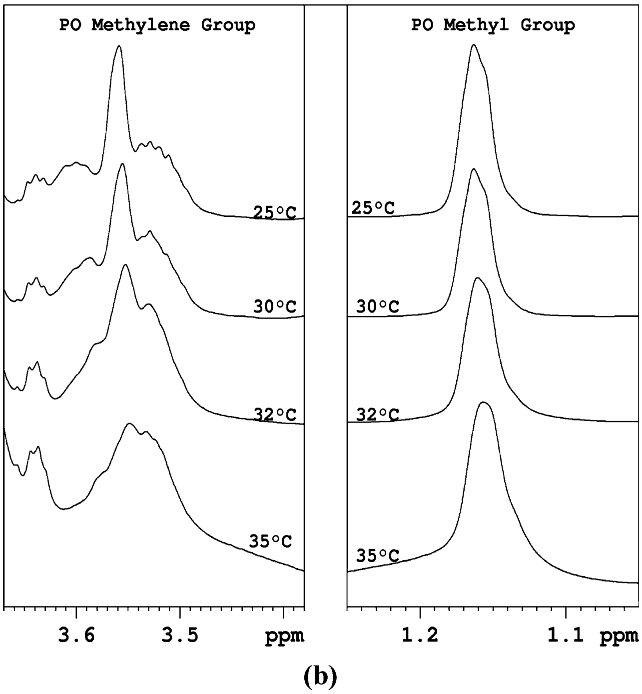


Fig. 5 **a** NMR signals for the PO (methyl) and PO (methylene) groups of 2% L64 as a function of urea concentration recorded at 35 °C. **b** NMR signals for the PO (methyl) and PO (methylene) groups of 2% L64 in the absence of urea as a function of temperature

shift. We found that urea behaves opposite to the temperature. Urea acts as water structure maker and facilitates the H bonding between the water molecules. The addition of urea enhances both the hydration layer of PEO and PPO segments and thus shifts all the NMR signals to higher ppm values. The spectral profiles associated with the micelle formation for L64 solution are moved to higher temperature by the addition of urea, which means that the addition of urea can shift L64 from micellar state to unimer state, that is, a demicellization process of block copolymer can be induced by adding urea [41].

The fluorescence spectroscopy provides important details on the micellar characteristics of the copolymer solution. Photoluminescence probes, e.g., pyrene, are capable of providing microscopic information concerning the nature of micellar aggregates in aqueous solution. The change in the (I_1/I_3) ratio in pyrene spectra provides better insight about the micropolar changes in the micellar core. A change in the microenvironment of the probe molecule can give an idea about the structural changes in molecular assemblies. Being very less soluble in water, pyrene gets partitioned in the hydrophobic core region of the molecular aggregate [42]. Now, it is a well-known fact that the ratio of the first and third vibronic peak (I_1/I_3) of the fluorescence emission spectra of pyrene is very sensitive to polarity of the solvent employed [43]. We have measured the polarity ratio (I_1/I_3) for pyrene spectra in 2% L64 solutions in water and urea solutions (0–6 M), shown in Fig. 6. The I_1/I_3 ratios are reported in the temperature range 10–55 °C. The CMT was obtained for each of these systems by intersection between the two lines, when the I_1/I_3 ratio starts to remain almost constant. It was observed that with the addition of urea, the temperature correlated with the micelle aggregation shifts to higher temperature. Urea clearly decreases the thermodynamic driving force for the hydrophobic interaction and is thus a potent destabilizer of copolymer structure. Hydrophobic interaction is the driving force for the micellization [44]; thus, it should be anticipated that increasing the urea concentration will increase both the CMT and CMC of block copolymer. Earlier studies have shown that surfactants stabilize in the aqueous urea solution which shifts the micellization to higher temperature [45]. Urea acts here as a salting-in agent facilitating more and more hydration of the PEO segment in the region. Micellization is a phenomenon due to the occurrence of hydrophobic forces. The weakness of this force (due to presence of urea) requires more heat for the increase of the hydrophobicity, which results in the elevation of the CMT. The higher the urea concentration, the greater the CMT of Pluronic solution. The CMTs obtained for 2% L64 in the absence of urea and in 4 M urea by FTIR and fluorescence were shown in Fig. 7a,b. The CMTs measured as a function of urea, in agreement with the earlier studies, showed an increase on addition of urea. The CMT rises to 41 °C on addition of 6 M urea from initial (in absence of urea) value of 32.5 °C.

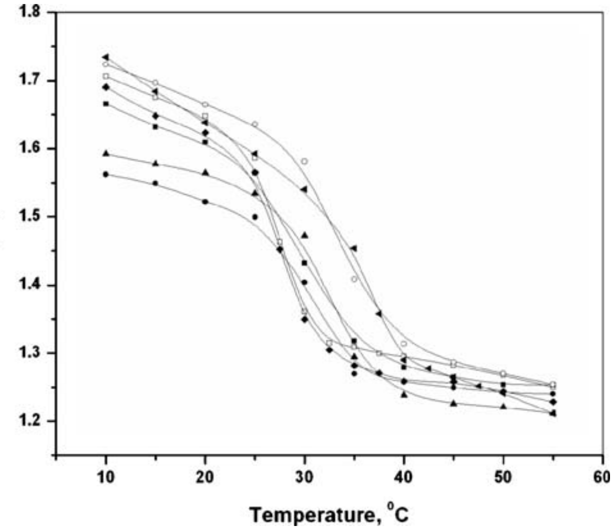


Fig. 6 Fluorescence vibronic peak ratio (I_1/I_3) vs. temperature for 2% L64 in different urea concentrations. (*open square*) 0 M, (*diamond*) 0.5 M, (*filled square*) 1 M, (*filled circle*) 2 M, (*triangle*) 3 M, (*open circle*) 4 M, (*left triangle*) 6 M

The DLS measurements provide useful information on the dimension of micellar aggregates based on the scattered intensity as a function of scattering wave vector "*q*". The diffusion coefficient was calculated with the help of decay rate ($\sim Dq^2$). Finally, the Stokes–Einstein equation was used to evaluate the hydrodynamic diameters of the micelles. The hydrodynamic diameter of the micelles formed by 10% L64 in urea–water solutions (0–4 M) was measured at two temperatures (40 °C and 50 °C) using DLS (Fig. 8). The exponential decay of the correlation of the intensity fluctuations, originating from the Brownian motion of the micelles, was measured during the DLS experiment. It is considered that the copolymer micelles exist as a hydrated sphere, and hence, the size (hydrodynamic diameter, D_h) is calculated using Stock–Einstein equation. Single mode of field intensity was observed in this regime for even 4 M concentration of added urea. At 40 °C in 10% solution in water, L64 exists as micelles with apparent hydrodynamic diameter of about 18 nm, which agrees well with earlier studies by Mata et al. [25]. We observed unimodal distribution in spherical regime at this temperature. The presence of urea shows only a slight increase in the micellar size particularly at high urea concentrations above 2 M. Though addition of urea is expected to decrease the aggregation number and should reflect in the hydrodynamic size, an opposite effect of urea that makes the water containing urea a better solvent for the PEO was observed (that would increase the shell thickness); this behavior is not unusual. At 50 °C, L64 in water shows micelles of

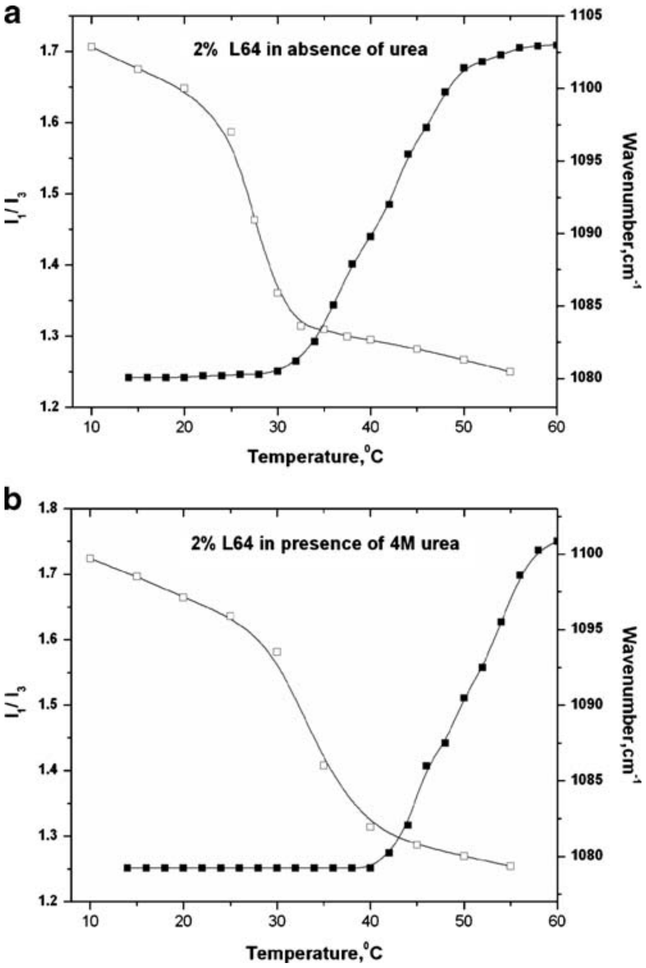


Fig. 7 **a** FTIR and fluorescence spectral changes for 2% L64 in the absence of urea in the temperature range 10–60 °C. **b** FTIR and fluorescence spectral changes for 2% L64 in presence of 4 M urea in the temperature range 10–60 °C

hydrodynamic size 50 nm diameter which can be expected at higher temperature. The presence of urea reverses this trend, and large L64 micelles gradually transform to smaller spherical micelles showing a decrease in size. Such decrease in micelles size is due to the presence of salting-in additive which influences the CP and CMT in the same way. Unimodal distribution of intensity was observed in this region as well. Our earlier report [25] had mentioned ellipsoidal micelles in 2 wt.% L64 solution at 40 °C. Here, we expect dimensionally higher micelles at experimental concentration and temperature. The D_h values were found to decrease with gradual increase in urea concentration. At 4 M urea concentration in the solution, D_h reached as low as 22 nm. The decrease in size is attributed to decrease in aggregation number. Due to bigger size of urea molecule in comparison to that of water's, we would expect the average cross-sectional area of the PEO molecule to increase with the addition of urea at a fixed temperature, thus effectively increasing steric repulsions between the PEO blocks; this would then lead to a decrease in the micellar size. Earlier studies [2, 19–22] on the interaction of urea with surfactants have shown that urea acts as structure maker for water molecule, and its presence is likely to increase dipole moment of water. As a result, faster hydration of the PEO moiety outside the micelle aggregate takes place. Urea replaces some of the water molecules from the hydration layer of the PEO segment. Urea molecules, being larger in size (approximately 2.5 times) than water molecules, would increase the steric repulsion between the PEO groups and thus contribute to the reduction in aggregation number [2, 19, 21] (Fig. 8).

Conclusion

The effect of urea on the demicellization of PEO/PPO/PEO block copolymers in aqueous solution was studied by different techniques. The extensive studied were carried out on L64–urea system. It is found that urea increases the CMT, CP, and micellar transition temperature of L64, which was confirmed by viscosity and DSC. Here, urea, working as salting-in additives, enhances the demicellization and tries to accumulate water molecules surrounding copolymer micelles. Urea was found to affect the micelles stability and decrease their size, which is supported by DLS measurements. The micelles show growth near the cloud point, but this transition is suppressed by urea, which is proven by DSC and viscometry. The present study is expected to offer useful information about the effect of urea on solution behavior of polymeric surfactant L64. Strong temperature-dependent micellization and micellar transitions in L64 solutions shift to higher temperature in the presence

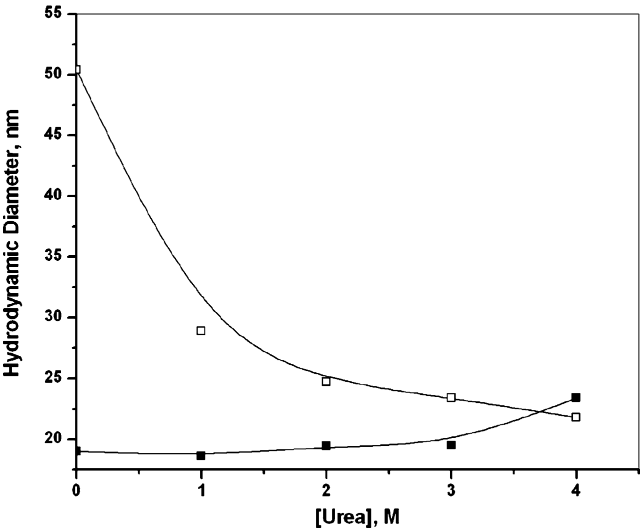


Fig. 8 Hydrodynamic diameter (D_h) obtained for 10% L64 in various concentrations of urea (0–4 M) at two different temperatures: 40 °C (*filled square*) and 50 °C (*open square*)

of urea, which can be tuned to obtain desired properties in copolymer solutions used for certain applications.

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References

1. Acharya KR, Bhattacharya SC, Moulik SP (2000) J Mol Liq 85:87
2. Alexandridis P, Athanassiou V, Hatton TA (1995) Langmuir 11:2442
3. Abu-Hamdiyyah M, Al-Mansour L (1979) J Phys Chem 83:2236
4. Kumar S, Khan ZA, Parveen N, Kabir-ud-Din (2005) Colloids Surf A: Physicochem Eng Aspects 268:45
5. Roy S, Dey J (2005) J Colloid Interface Sci 290:526
6. BASF Corp. (1989) Pluronic and tetronic block copolymer surfactants. Technical Brochure
7. Price C (1983) Micelle formation of block copolymers in organic solvents. Pure Appl Chem 55:1563
8. Riess G, Hurtrez G, Bahadur P (1985) Encyclopedia of polymer science and engineering, 2nd edn. Wiley, New York
9. Bahadur P, Riess G (1991) Tenside Surfactants Deterg 28:173
10. Alexandridis P, Hatton TA (1995) Colloids Surfaces 96:1
11. Alexandridis P, Holzwarth JF (2000) Curr Opin Colloid Interface Sci 5:312
12. Yang L, Alexandridis P, Steytler DC, Kositza M, Holzwarth JF (2000) Langmuir 16:8555
13. Hurter PN, Hatton TA (1992) Langmuir 8:1291
14. Alexandridis P (1996) Curr Opin Colloid Interface Sci 1:490
15. Suzuki K, Saito Y, Tokuoka Y, Abe M, Sato T (1997) J Am Oil Chem Soc 74:55
16. Wetlaufer DB, Malik SK, Stoller L, Coffin RL (1964) J Am Chem Soc 86:508
17. Frank HS, Franks F (1968) J Chem Phys 48:4746
18. Nozaki Y, Tanford C (1964) J Biol Chem 238:4074
19. Briganti G, Puvvada S, Blankschtein D (1991) J Phys Chem 95:8989
20. DasGupta PK, Moulik SP (1989) Colloid Polym Sci 267:246
21. Capponetti E, Causi S, De Lisi R, Floriano MA, Milioto S, Triolo R (1992) J Phys Chem 96:4950
22. Han SK, Lee SM, Kim M, Schott H (1989) J Colloid Interface Sci 132:444
23. Chu B, Zhou Z (1996) Physical chemistry of polyoxyalkylene block copolymer surfactants in nonionic surfactants. In: Nace VM (ed) Surfactant science series. Marcel Dekker, New York, pp 60–67
24. Christov NC, Denkov ND, Kralchevsky PA, Ananthapadmanabhan KP, Lips A (2004) Langmuir 20:565
25. Mata JP, Majhi PR, Guo C, Liu HZ, Bahadur P (2005) J Colloid Interface Sci 292:548
26. Kabir-ud-Din, Kumar S, Aswal VK, Goyal PS (1996) J Chem Soc Faraday Trans 92:2413
27. Bershtein AV, Egorov VM (1994) Differential scanning calorimetry of polymers. Ellis Horwood, London
28. Berne BJ, Pecora R (1976) Dynamic light scattering: with applications to chemistry, biology and physics. Wiley, New York
29. Zana R (2000) Fluorescence studies of amphiphilic block copolymers in silution. In: Alexandridis P, Lindman B (eds) Amphiphilic block copolymers. Self-assembly and applications. Elsevier, Amsterdam, p 221
30. Wanka G, Hoffman H, Ulbricht W (1994) Macromolecules 24:4145
31. Ruiz C, Sanchez F (1994) J Colloid Interface Sci 165:110
32. Carvalho BL, Briganti G, Chem SH (1989) J Phys Chem 93:4282
33. Kumar S, Sharma D, Ghosh G, Kabir-ud-Din (2005) Langmuir 21:9446
34. Glatter O, Scherf G, Schillen K, Brown W (1994) Macromolecules 27:6046
35. Wanka G, Hoffman H, Ulbricht W (1990) Colloid Polym Sci 268:101
36. Armstrong JK, Chowdhry BZ, Snowden MJ, Leharne SA (1998) Langmuir 14:2004
37. Zhang ZQ, Liang YQ (1995) J Colloid Interface Sci 169:220
38. Wang W, Li LM, Xi SQ (1993) J Colloid Interface Sci 155:369
39. Ma JH, Guo C, Tang YL, Wang J, Zheng LL, Liang XF, Chen HZ (2006) J Colloid Interface Sci 299:953
40. Nivaggioli T, Tsao B, Alexandridis P, Hatton TA (1995) Langmuir 11:119
41. Ma JH, Guo C, Tang YL, Chen L, Bahadur P, Liu HZ (2007) J Phys Chem 111:5155
42. Kalyanasundaram K, Thomas JK (1977) J Am Chem Soc 99:2039
43. Damas C, Carre MC, Viriot ML, Loehon P (1997) Colloid Polym Sci 275:364
44. Tanford C (1980) The hydrophobic effect: formation of micelles and biological membranes. Wiley Interscience, New York
45. Singh PK, Ahluwalia JC (1989) In: Mittal KL (ed) Surfactant in solution, vol 3. Plenum, New York, p 277