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# Growth and Interaction of the Tetronic 904 Micelles in Aqueous Alkaline Solutions

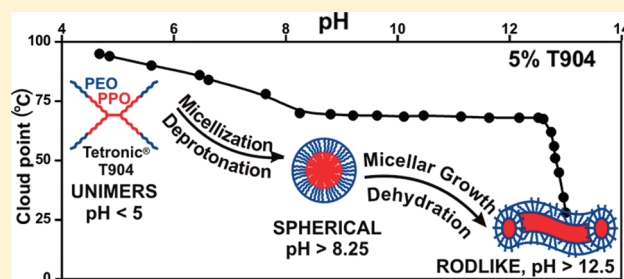
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**ABSTRACT:** The influence of sodium hydroxide (NaOH) on the aggregation characteristics of the Tetronic 904 (T904) has been studied in the aqueous medium by dynamic light scattering (DLS), small angle neutron scattering (SANS), and viscometry methods. This polyethylene oxide (PEO)–polypropylene oxide (PPO) based X-shaped triblock copolymer shows pH sensitive aggregation characteristics due to the presence of a central amine group attached with the PPO block. The aqueous micellar solutions of this copolymer have been found to show a large increase in the room temperature (30 °C) relative viscosity with an increase in NaOH concentration, before they undergo phase separation at 1.25 M NaOH concentration. SANS and DLS studies ascribe this behavior to a sphere to rod growth of the copolymer micelles on approaching the cloud points of the copolymer solutions. DLS studies show that the observed micellar growth is accompanied by critical scattering due to the onset of an attractive intermicellar interaction. To understand the role of NaOH in inducing the observed micellar shape transition, we have also studied the effect of NaOH on the micellar solutions of Pluronic P84, which does not show pH sensitivity due to the absence of the central amine group but has the same weight fraction of the PEO block (40%) as that of T904. Quite interestingly, the P84 micelles too have been found to undergo a similar room temperature sphere to rod shape transition in the presence of NaOH. The observed growth and interaction of the Tetronic micelles have thus been attributed to the dual effects of NaOH in influencing the aggregation characteristics of the Tetronic molecules. On one hand, it stabilizes these micelles by the deprotonation of the copolymer molecules, and on the other hand, its dehydrating effect on the copolymer molecules promotes the onset of micellar growth and intermicellar attractive interaction at the room temperature. The observed results are the first of their kind in the aqueous Tetronic system.



## INTRODUCTION

The polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) copolymers, namely, the linear chain Pluronic<sup>1–3</sup> and the X-shaped Tetronics<sup>4–10</sup> (Figure 1), have been the subject of interest of researchers for over two decades due to their wide range of applications and rich structural polymorphism. In the aqueous medium, strongly temperature dependent and differential solubility characteristics of the PEO and PPO blocks play an important role in determining the self-assembly characteristics of these copolymers.<sup>11–14</sup> At low temperature, the PPO and PEO blocks are soluble in water and the molecules of both of these copolymers remain singly dissolved as unimers. At the critical micellar temperature (CMT), they start forming micelles comprising a hydrophobic core containing the PPO blocks and a hydrated corona containing the PEO blocks.<sup>11–14</sup> Since the solubility of the PEO block decreases with an increase in temperature above the CMT, the micelles undergo restructuring to increase their aggregation number and core size, and to decrease their degree of hydration.<sup>15–17</sup> In the case of some of the Pluronic, such micellar restructuring with an increase in temperature leads to a sphere-to-rod micellar shape change

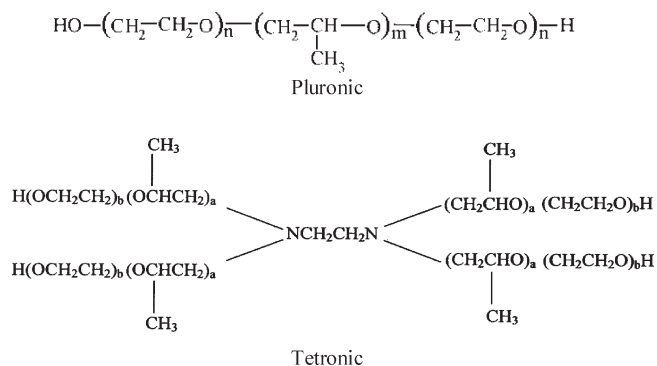
before the copolymer solutions undergo phase separation at the cloud point (CP).<sup>18–23</sup>

The temperature dependence apart, the X-shaped Tetronics also show strong pH dependence in their self-assembly characteristics due to the presence of the central ethylene diamine unit in their molecules.<sup>9,10,13,24,25</sup> The pH dependence of the self-assembly characteristics makes the Tetronics more attractive for the drug delivery applications vis-à-vis the Pluronic due to the possibility of modulating the micellar structure at physiological conditions.<sup>9,10,13,24,25</sup> In the acidic pH, the formations of mono- and diprotonated forms of this unit impede the micelle formation process due to the reduced hydrophobicity of the micellar core comprising the hydrophobic PPO blocks.<sup>9,10</sup> At the alkaline pH on the other hand, the micelle formation is facilitated due to the disappearance of the protonated forms and the subsequent enhancement of the hydrophobicity of the micellar core.<sup>9,10</sup> Detailed structural studies on the micelles of these compounds under alkaline conditions have, however, not been reported so

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**Figure 1.** General representation of Pluronic and Tetronic molecules.

far. In view of this, we have carried out a systematic study on the size and shape of the Tetronic 904 micelles in the presence of a strong alkali, NaOH. We observed that micelles of this Tetronic copolymer not only grow to show a sphere-to-rod shape transition but also exhibit onset of an attractive intermicellar interaction en route to phase separation upon addition of NaOH. A comparison of these results with the influence of NaOH on the micellar characteristics of Pluronic P84 suggests that, though the Tetronic micelles get stabilized with an increase in pH in the presence of NaOH, the observed growth of these micelles is brought about by the dehydrating effects of NaOH on the copolymer molecules.

## EXPERIMENTS

**Materials and Sample Preparation.** The copolymers Tetronic 904 and Pluronic P84 were procured from BASF Corp. Parsippany, NJ, USA, and sodium hydroxide was purchased from s-d fine-chem limited, India. The copolymer solutions at different NaOH concentrations were prepared by weighing required amounts of water obtained from a Millipore Milli-Q purification system, the copolymer, and NaOH and keeping them in a refrigerator in tightly closed glass stoppered vials overnight.

## METHODS

**Viscometry.** The absolute viscosities of the solutions at room temperature (25 °C) were measured in a temperature controlled water bath by using size 50, 150, and 350 calibrated cannon Ubbelohde viscometer<sup>26</sup> with 0.0041, 0.03983, and 0.2775 centistokes/sec viscometer constants. The measured flow times of the solutions in seconds were multiplied with the viscometer constant to get the kinematic viscosity of the solutions in centistokes. The uncertainties in the flow time have been found to remain within  $\pm 15$  s. The kinematic viscosities obtained were then multiplied by the density of water to obtain the viscosity of the micellar solutions in centipoise. The relative viscosities at different temperatures were calculated by dividing the absolute viscosities by the viscosity of water at respective temperatures.

**Dynamic Light Scattering (DLS).** DLS measurements of the solutions were performed using a Malvern 4800 Autosizer employing a 7132 digital correlator. The light source was a 25 mW He–Ne laser operated at a 633 nm wavelength. The average decay rate was obtained by analyzing the electric field autocorrelation function  $g^1(\tau)$  vs time data using a modified cumulants method or a stretched biexponential equation.<sup>27–30</sup> The modified cumulants method overcomes the limitations of

cumulants analysis to fit the data at long correlation time or large polydispersity.<sup>31</sup> The decay rates obtained from the analyses of the correlation function data were used to calculate the diffusion coefficients and subsequently the apparent equivalent hydrodynamic radii of the micelles by using the Stokes–Einstein relationship.

**Small Angle Neutron Scattering (SANS).** SANS measurements were carried out on the samples prepared in D<sub>2</sub>O at the SANS facility at the DHRUVA reactor, Trombay. The mean incident wavelength was 5.2 Å with  $\Delta/\lambda = 15\%$ . The neutron scattering cross sections were measured in the scattering vector ( $q$ ) range of 0.017–0.3 Å<sup>−1</sup>. The measured SANS data were corrected for the background, the empty cell contributions, and the transmission and were placed on an absolute scale using standard protocols. Correction due to the instrumental smearing was taken into account throughout the data analysis.<sup>32</sup>

**Data Analysis.** The differential scattering cross section per unit volume ( $d\Sigma/d\Omega$ ) of monodisperse micelles can be written as<sup>33,34</sup>

$$d\Sigma/d\Omega = NF_{\text{mic}}(q)S(q) + B \quad (1)$$

$N$  is the number density of the micelles, and  $B$  is a constant term that represents the incoherent background scattering mainly from the hydrogen atoms present in the sample.  $F_{\text{mic}}(q)$  is the form factor characteristic of specific size and shape of the scatterers, and  $S(q)$  is the structure factor that accounts for the interparticle interaction. The Tetronic micelles can be considered as a core–shell particle with different scattering length densities of the core and the shell. The structure of these micelles is described using a model consisting of hydrated PEO chains attached to the surface of the hydrophobic core comprising the PPO blocks.<sup>33–35</sup> The shell is described as consisting of non-interacting Gaussian polymer chains, and these chains are assumed to be displaced from the core (or else the mathematical approximations will not work as the chains overlap each other and the core); i.e., a mushroom polymer configuration is assumed. Nonpenetration of the chains into the core region is mimicked by moving the center of mass of the chains by a distance  $R_g$  away from the surface of the core, where  $R_g$  is the radius of the gyration of the chains. The form factor of the micelles  $F_{\text{mic}}(q)$  comprises four terms: the self-correlation of the core, the self-correlation of the chains, the cross term between the core and chains, and the cross term between different chains. The scattering length densities of the D<sub>2</sub>O and the shell are quite close because of the presence of a considerable amount of D<sub>2</sub>O in the shell. The core being hydrophobic, however, will have significantly different scattering properties compared to the shell due to the widely different scattering length densities of hydrogen and deuterium. This model has been successfully used to fit the SANS data of aqueous micellar solutions of different Pluronics. The form factors for spherical and ellipsoidal micelles were used as formulated by Pedersen.<sup>33–35</sup> The interparticle structure factor  $S(q)$  for the spherical block copolymer micelles is usually captured by the analytical solution of the Ornstein–Zernike equation with the Percus–Yevick approximation, employing hard sphere interaction.<sup>36</sup>

In the case of polydisperse micelles, eq 1 can be written as

$$d\Sigma/d\Omega(q) = \int d\Sigma/d\Omega(q, R_c) f(R_c) dR_c + B \quad (2)$$

The polydispersity in the micellar size ( $R = R_c$ ) has been accounted for by a Schultz distribution, as given by the equation

$$f(R_c) = [(z+1)/R_{cm}]^{z+1} R_c^z \exp[-(z+1)/R_{cm}] R_c [1/(\Gamma(z+1))] \quad (3)$$

where  $R_{cm}$  is the mean value of the distribution and  $z$  is the width parameter. The polydispersity of this distribution is given by  $\Delta R_c/R_{cm} = 1/(z+1)^{1/2}$ .

The analyses of the data were carried out by using  $R_g$ ,  $R_{gs}$ ,  $R_{hs}$ ,  $\phi$ , and  $Z$  as variables. These parameters were optimized by means of a nonlinear least-squares fitting program in Fortran.<sup>37</sup>

**Theoretical Modeling of the Viscosity Data.** For a dilute micellar solution, intermicellar interaction is negligibly small. However, for a concentrated solution, micellar interaction and distribution must be taken into consideration to interpret the experimental observations. The adhesive hard sphere model of Baxter and its variant are widely used to model concentrated micellar solutions.<sup>38–40</sup> In these model systems, attractive interaction between two spherical particles has been introduced by considering a thin adhesive layer on top of the hard core of the particle, the detailed formulation of which is available in the literature.<sup>38–40</sup> The structure factor for the adhesive hard sphere system is a function of micellar volume fraction, attractive potential ( $\Omega$ ) or stickiness parameter ( $\tau^{-1}$ ), and the fractional surface layer thickness ( $\varepsilon$ ).<sup>39</sup> The calculations of the viscosity were carried out assuming the fractional layer thickness  $\varepsilon$  to be small but finite, and the detailed analytical expression of the structure factor for this is given in the literature.<sup>39</sup>

The relative viscosity ( $\eta_r$ ), defined as the ratio of the solution viscosity to the solvent viscosity, generally consists of contributions arising from hydrodynamic as well as interparticle interactions and can be written as<sup>41,42</sup>

$$\eta_r = \eta_{HD} + \eta_I \quad (4)$$

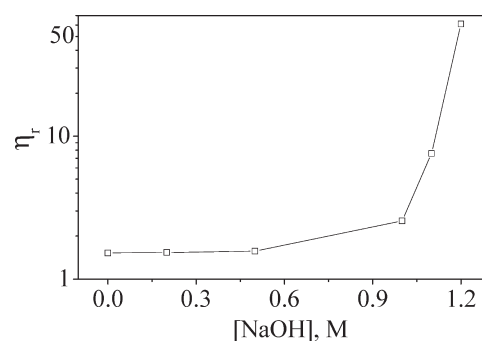
where  $\eta_{HD}$  is the hydrodynamic viscosity, which is calculated here using the Batchelor–Green equation, i.e.,  $\eta_{HD} = 1 + 2.5\phi + 5.2\phi^2$ , with  $\phi$  being the volume fraction of the micellar solution. In the above equation,  $\eta_I$ , the contribution arising from intermicellar interaction, is expressed in terms of the static structure factor  $S(Q)$ :

$$\eta_I = \frac{\chi}{40\pi} \int_0^\infty dQ Q^2 d(Q) \frac{[S'(Q)]^2}{S(Q)} \quad (5)$$

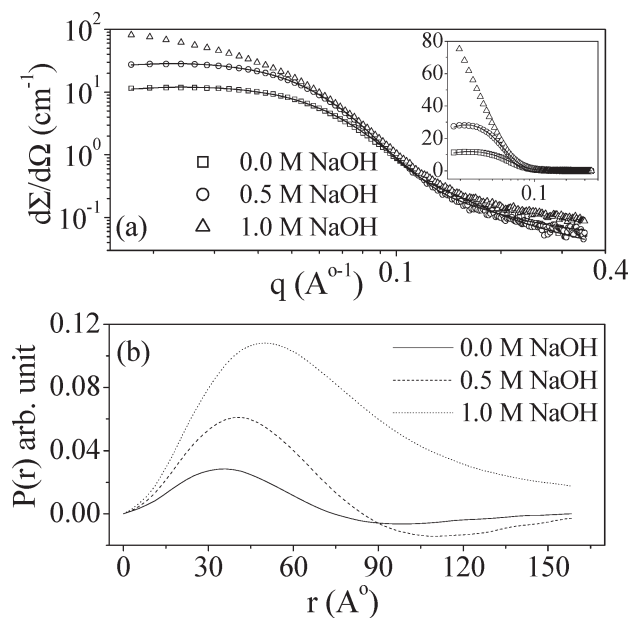
where  $\chi$  is the value of the pair correlation function at contact,  $d(Q) = 1 - j_0(Q) + 2j_2(Q)$ , with  $j_i(x)$  being the  $i$ th order spherical Bessel function,<sup>39</sup> and  $S'(Q)$  is the first derivative of the structure factor  $S(Q)$  with respect to  $Q$ .

## RESULTS AND DISCUSSION

The viscosities of the micellar solutions of PEO–PPO based copolymers like Pluronics are modeled considering the micellar solutions as hard sphere dispersions.<sup>39,43,44</sup> As per this concept, the viscosities of the copolymer solutions are determined primarily by the concentration of the spherical micelles and the interaction between them.<sup>39</sup> The effect of attractive intermicellar interaction on the viscosity of the copolymer solutions can be accounted for by the adhesive hard sphere model, which envisages the presence of a thin adhesive layer at the surface of the hard spheres in the form of an attractive potential well. This model suggests that the viscosity of the micellar solution is a



**Figure 2.** Relative viscosity ( $\eta_r$ ) of 5% T904 solution as a function of NaOH concentration recorded at 30 °C.



**Figure 3.** (a) SANS patterns of 5% aqueous T904 solutions at 30 °C as a function of NaOH concentration. The inset shows the plots in the linear scale of neutron scattering cross section, and the solid lines for 0.0 and 0.5 M NaOH concentrations represent the fit to the data using spherical form factors. (b) The corresponding pair distance distribution function  $[P(r)]$  plots as a function of NaOH concentration.

sensitive function of intermicellar interaction and increases quite significantly in the presence of strong intermicellar attractive interaction. These two factors, i.e., the concentration and the interaction of the micelles apart, a sphere-to-rod growth of the micelles also has a profound impact on the viscosity of these copolymer solutions. Such a shape transition of the micelles can lead to an increase in the viscosity of the copolymer solutions by quite a few orders of magnitude.<sup>18–21</sup>

To understand the effect of NaOH on the viscosity of the T904 solution, we have studied the variation of the viscosity of the 5% copolymer solution as a function of NaOH concentration (Figure 2). It is observed that the viscosities of these copolymer solutions undergo a marked increase above 1 M NaOH concentration until the solutions phase separate at 1.25 M NaOH concentration. As has been discussed in the previous section, the observed increase in the viscosity of the copolymer solution in the presence of NaOH can result from either a micellar shape change or an onset of attractive intermicellar interaction.

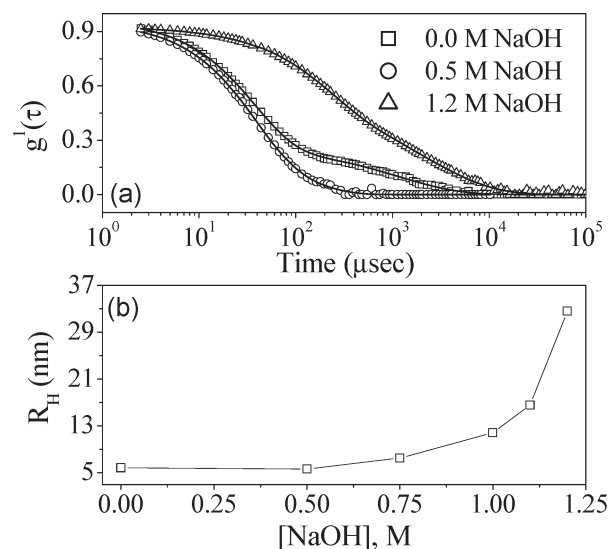


**Table 1.** The Core Radius ( $R_c$ ), the Aggregation Number ( $N_{agg}$ ), the Radius of Gyration of the Chains ( $R_g$ ), the Micellar Volume Fraction ( $\phi$ ), the Hard Sphere Radius ( $R_{HS}$ ), and the Polydispersity ( $\Delta R_c/R_{cm}$ ) of the Micelles in 5% T904 Solutions at 30 °C

| NaOH conc (M/Lit) | $R_c$ (nm)      | $N_{agg}$ | $R_g$ (nm)      | $\phi$           | $R_{HS}$ (nm)   | $\Delta R_c/R_{cm}$ |
|-------------------|-----------------|-----------|-----------------|------------------|-----------------|---------------------|
| 0.0 M             | $2.55 \pm 0.01$ | 11        | $0.62 \pm 0.20$ | $0.041 \pm 0.01$ | $5.76 \pm 0.03$ | $0.26 \pm 0.01$     |
| 0.5 M             | $3.18 \pm 0.01$ | 20        | $0.67 \pm 0.15$ | $0.050 \pm 0.01$ | $6.36 \pm 0.04$ | $0.24 \pm 0.01$     |

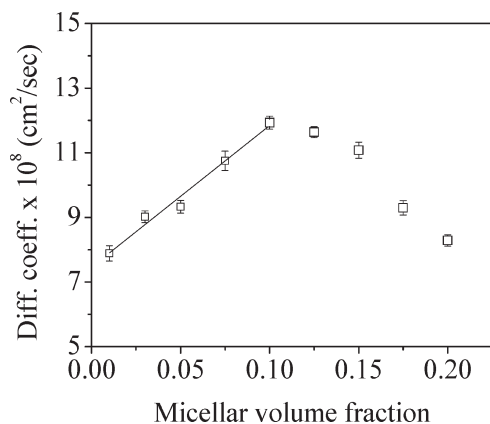
To understand the mechanism behind the observation, we have carried out SANS and DLS measurements on the 5% copolymer solutions as a function of NaOH concentration.

Figure 3a shows the SANS plots of 5% Tetronic solution at 0.0, 0.5, and 1.0 M NaOH concentration. The presence of NaOH leads to a significant increase in the scattering intensity at low  $q$ -values. This observation could result from either micellar growth or the presence of attractive intermicellar interaction, or even an interplay of both of these factors.<sup>45</sup> Analysis of the data of the pure solution based on the spherical form factor shows that the micelles form with an aggregation number of 11 and with a volume fraction of 0.041 (Table 1). The micelles of this copolymer are expected to show a significant degree of micellar hydration due to the presence of about 40 wt % hydrophilic PEO block in the copolymer molecules.<sup>43</sup> The micellar volume fraction is thus expected to be significantly higher than the copolymer volume fraction, which is 0.05. Considering this, the obtained micellar volume fraction of 0.041 is suggestive of the presence of a significant amount of copolymer molecules in the unimer form. It has been shown in the literature that, at pH values close to 7, which is the experimental condition because of the use of Millipore grade water in the sample solution, a significant fraction of the copolymer molecules are in the mono- and diprotonated forms.<sup>9</sup> This factor, which increases the overall hydrophilicity of the copolymer molecules, could be responsible for the low aggregation number obtained by us as compared to those reported in the case of Pluronics having similar PEO weight fractions.<sup>30,46</sup> It has been reported that the fraction of these two protonated forms decreases with an increase in pH of the copolymer solutions.<sup>10</sup> In the present case, the analysis of the SANS data shows that, though the aggregation number of the micelles doubles upon addition of 0.5 M NaOH, the micellar volume fraction increases only marginally. This suggests that even under strongly alkaline conditions a significant fraction of the copolymer molecules do not get converted into micelles. As shown in Figure 3a, the presence of 1.0 M NaOH leads to a large increase in the scattering intensity and disappearance of the correlation peak (inset of Figure 3a), which arises due to intermicellar interaction. This could result from either a large growth of the copolymer micelles accompanied by a sphere-to-rod micellar shape change or the presence of large intermicellar attractive interaction.<sup>21,39</sup> If we consider it to arise due to the sphere-to-rod micellar growth, the determination of the size of the micelles will not be possible because of our limited  $q$  region of measurement. The reason is the large viscosity enhancement in the viscosity of copolymer solution shown in Figure 2 is suggestive of a large micellar growth with a high value of the aspect ratio. An accurate estimation of the size of these micelles will require SANS measurement up to much lower  $q$  values that could not be obtained in our instrument. The micellar parameters obtained from the DLS results as shown in the next section also support this conjecture. To understand about the micellar structure, we calculated the pair distance distribution functions [ $P(r)$ ] data for these plots obtained using the program

**Figure 4.** (a) Correlation function diagrams of 5% T904 solutions recorded at 30 °C and 130° scattering angle as a function of NaOH concentration. The solid lines represent fits to the data. (b) Hydrodynamic radius of the micelles in 5% T904 solutions as a function of NaOH concentration at 30 °C.

GENOM made by Svergun and A. Semenyuk.<sup>47,48</sup> As shown in Figure 3b, a significantly higher asymmetry in the  $P(r)$  plot in the presence of 1.00 M NaOH is a clear signature of the presence of a large anisotropy of the micelles in the form of a rodlike shape. This suggests that a sphere-to-rod micellar growth plays a role in the observed increase in the scattering intensity in the low  $q$  region.

Figures 4 and 5 show the DLS studies on the 5% Tetronic 904 solutions as a function of NaOH concentration at 30 °C. The evolution of the correlation function diagram with an increase in the alkalinity of the copolymer solution is shown in Figure 4a. In the absence of NaOH, the correlation function diagram shows a biexponential decay corresponding to the presence of two types of scattering species with widely different average sizes. Since the concentration of the copolymer taken is above its CMC,<sup>9,49</sup> one of these, and in particular the smaller one, is likely to be a micelle and the very large sized particles could be some kind of micellar clusters. The presence of such micellar clusters along with the micelles has earlier been observed in the aqueous Pluronic solutions above the CMC of the respective copolymers.<sup>50,51</sup> Their origin, though, has not been fully understood yet. Zhou and Chu<sup>52,53</sup> ascribed the presence of these aggregates to the compositional in-homogeneities of the copolymers. Liang et al. from their NMR studies, on the other hand, represented these aggregates as big swollen micelles in which both the corona and the core of the micelles remain heavily hydrated.<sup>54</sup> In all of these cases, however, the so-called micellar clusters start forming below the CMT of the copolymer solutions and slowly disappear as the temperature increases above the CMT. Considering that the



**Figure 5.** The variation of the micellar diffusion coefficient with micellar volume fraction at 1.1 M NaOH concentration. The solid line represents the fit to the data up to 0.1 volume fraction.

CMT of 5% T904 solution is 28.8 °C,<sup>46</sup> the observation of these aggregates at 30 °C, as shown in Figure 4a, is in accordance with those observed in the case of different Pluronics. Besides, the Tetronic micelles are protonated at the core but the micelles have been modeled as hard spheres with an overall charge neutrality,<sup>10,46</sup> and that is supported by the fact that the T904 solutions undergo phase separation above 70 °C. The results of the analysis of the plot based on a biexponential equation representative of the presence of two scattering species are shown in Figure 4b, where the hydrodynamic size of the micelle is plotted against the concentration of NaOH. As expected, the size of the smaller species obtained by the analysis is close to the size of the Tetronic 904 micelles reported in the literature.<sup>9</sup>

In the aqueous Tetronics system, the existence of mono- and diprotonated forms of the central diamine unit in the acidic pH impedes the process of the micelle formation.<sup>9</sup> The dissociation constants associated with these protonated forms are termed as  $K_{a1}$  and  $K_{a2}$ . With an increase in pH of the copolymer solution, the mono- and diprotonated forms start dissociating to convert to the un-ionized form at pH values of  $pK_{a1}$  and  $pK_{a2}$ , respectively.<sup>9,10</sup> Deprotonation of the Tetronic molecules facilitates micellization and leads to a decrease in their CMC and CMT. A decrease in CMT with an increase in the NaOH concentration is expected to reduce the cluster formation, and as can be seen in Figure 4a, the signature of the cluster formation in the correlation function diagram indeed reduces upon addition of NaOH and almost vanishes at 0.5 M NaOH concentration. Besides this, there is a significant growth of the micelles which is evident from the large shift in the correlation function plot to longer time scale at 1.2 M NaOH concentration. At this NaOH concentration, the copolymer solution shows large viscosity and quite interestingly the correlation function plot again becomes biexponential. The change in the nature of the plot could arise due to two reasons, namely, the entanglement of the rodlike micelles in case the micelles have undergone a sphere-to-rod shape change<sup>28,29</sup> or the presence of big micellar clusters because of intermicellar attractive interaction.<sup>39,44</sup> Both of these factors can lead to a shift in the representative correlation function diagram of the micelles and an increase in the viscosity of the copolymer solution.<sup>39,40</sup> The calculation of the micellar size in the case of the biexponential plot at 1.2 M NaOH concentration was done by using a stretched biexponential

equation as the following:

$$g^{(1)}(t) = A_f * \exp(-t/\tau_f) + A_s * \exp[-(t/\tau_s)^\beta] \quad (6)$$

where  $A_f$  and  $A_s$  are the amplitudes for the fast and slow relaxation modes corresponding to the relaxation times  $\tau_f$  and  $\tau_s$ , respectively.<sup>28,29</sup> The relaxation time for the fast mode is associated with the diffusion of the micelles, and that of the slow mode can be ascribed either to coupling between concentration fluctuation or stress relaxation in entangled rod-like micelles. The presence of micellar clusters arising due to attractive intermicellar attractive interaction also contributes to the second mode.<sup>44</sup> The exponent  $\beta$  ( $0 < \beta \leq 1$ ) is inversely proportional to the width of the distribution of the relaxation times of the slow mode. The variation of the apparent micellar size with an increase in the NaOH concentration is shown in Figure 4b. The apparent hydrodynamic size first shows a slow rise up to 1.0 M NaOH but then shows a sharp increase after that until the copolymer solution phase separates at 1.25 M NaOH concentration. This behavior is similar to what is observed in the viscosity behavior, where the rate of increase in the relative viscosity of the copolymer solutions becomes noteworthy only above 1 M NaOH concentration.

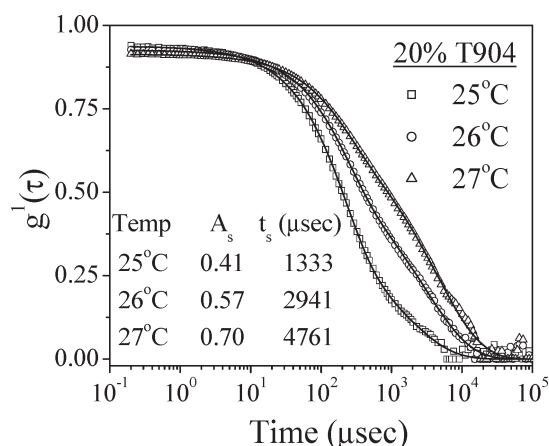
To understand more about the observed NaOH induced increase in viscosity of the copolymer solution and the consequent increase in the apparent size of the copolymer micelles, we have studied the variation of the diffusion coefficient of the micelles as a function of micellar volume fraction at 1.1 M NaOH concentration (Figure 5). The micellar volume fraction at this NaOH concentration has been approximated as equal to the copolymer volume fraction in the light of the SANS studies, which showed that in the case of 5% copolymer solution the micellar volume fraction is equal to the copolymer volume fraction at NaOH concentrations as high as 0.5 M. To calculate the diffusion coefficients, the correlation function plots were recorded at 2 °C below the cloud points of the respective solutions, which decreased by 10 °C as the copolymer concentration increased from 1 to 20%. To compensate for the effect of this change in measurement temperature and the associated change in the viscosity of water on the diffusion coefficient of the micelles, the correlation function data recorded were normalized with respect to 300 K based on the following equation:<sup>28</sup>

$$t_{\text{norm}} = t \frac{T}{300} \frac{\eta_{300}}{\eta_T} \quad (7)$$

Figure 5 shows that the diffusion coefficient obtained from the normalized data first increases up to a volume fraction value of 0.10 (10% copolymer concentration) and then decreases up to the maximum copolymer concentration studied (20%). This is different from that exhibited by aqueous Pluronic P123 solutions, which show a monotonic increase in diffusion coefficient up to a micellar volume fraction of as high as about 0.5.<sup>21</sup> In the case of hard sphere dispersions, the diffusion coefficient increases with volume fraction ( $\phi$ ) and its variation can be expressed as

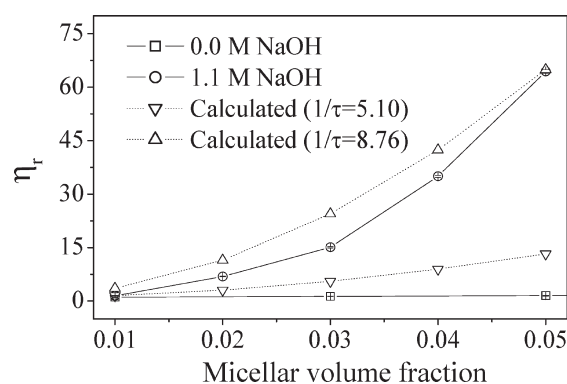
$$D_{\text{eff}} = D_0(1 + k_0\phi) \quad (8)$$

where  $D_{\text{eff}}$  is the effective diffusion coefficient at any volume fraction,  $\phi$ ,  $D_0$  is the diffusion coefficient at infinite dilution, and  $k_0$  is the virial coefficient that has a value of 1.56 for colloids with hard sphere interaction. In the case of micelles, the virial coefficient increases significantly in the presence of micellar hydration and a sphere-to-rod shape change of the micelles.<sup>21</sup>



**Figure 6.** Plots of the correlation function data of 20% T904 solution in the presence of 1.1 M NaOH as a function of temperature. The solid lines represent fits to the data.

These two factors apart, the presence of an attractive intermicellar interaction as described in the literature based on the adhesive hard sphere model proposed by Baxter<sup>38</sup> also influences the dependence of the diffusion coefficient on the micellar volume fraction in a significant way. As has recently been shown, in the presence of a strong intermicellar attractive interaction, the diffusion coefficient decreases with an increase in the volume fraction.<sup>40,55,56</sup> The plot of the diffusion coefficient shown in Figure 5 does not match any of these distinct possibilities. The observation of maxima is, on the other hand, suggestive of the presence of two competing and opposite effects of the repulsive as well as attractive intermicellar interactions. The simultaneous presence of these two micellar characteristics has earlier been observed in the aqueous solutions of Pluronic L64 and another polyethylene oxide based nonionic surfactant near their cloud points.<sup>44,45</sup> In both cases, the observed viscosity enhancement on approaching the cloud point has primarily been attributed to sphere-to-rod micellar growth. The presence of the attractive intermicellar interaction leads to the observation of critical scattering just below the cloud point. Corti and Degiorgio<sup>57</sup> and Zulauf and Rosenbusch<sup>58</sup> observed similar critical behavior in different oxyethylene based nonionic micellar systems and explained them based on the formation of large but loosely bound statistical clusters due to the presence of weak intermicellar attractive interaction. These clusters, which include both micelles and water, are formed when micelles are correlated over a distance much larger than the micellar size, and can be probed by dynamic light scattering along with the individual micelles.<sup>57,58</sup> The presence of weak intermicellar attractive interaction has been proposed because of the fact that the presence of a strong attractive interaction would result in the observation of percolation due to the formation of stable and compact clusters, instead of loosely bound ones. In the present case, the analysis of the diffusion coefficient data shows that, apart from the appearance of slow moving species, there is significant growth of the faster moving micelles as the temperature approaches the cloud point. The initial increase in the diffusion coefficient (a positive  $k_0$ ) has been fitted based on eq 8 to obtain the value of  $D_0$ , i.e., the diffusion coefficient at infinite dilution.  $D_0$  and the corresponding  $R_{H,0}$ , i.e., the hydrodynamic radius at infinite dilution, calculated based on the Stokes–Einstein equation, were found to be  $7.46 \times 10^{-8}$  cm<sup>2</sup>/s and 37.2 nm, respectively. For the present block



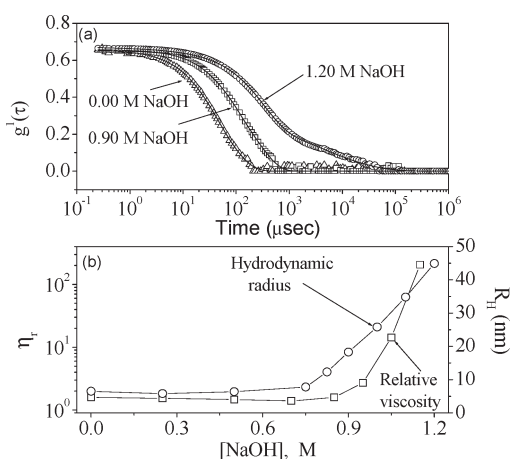
**Figure 7.** Comparison of the relative viscosity ( $\eta_{rel}$ ) vs micellar volume fraction plots in the presence and absence of 1.1 M NaOH and the plots calculated based on the adhesive hard sphere model.

copolymer, as the maximum extended length of PO and EO chains is much less than 37.2 nm, it is unrealistic to have a spherical micelle of about 37 nm radius. This suggests that the micelles of an apparent radius of 37.2 nm may have either a prolate or an oblate ellipsoidal shape. At a given volume fraction, the relative viscosity of a suspension is sensitive to the shape of the colloid. A comparison of the shape factors for spheres and prolate and oblate ellipsoids suggests that, having the same equivalent hydrodynamic diameter and volume fraction, the relative viscosity of the solutions with prolate ellipsoids will be much higher than that with the oblate ellipsoids.<sup>59</sup> Thus, it is very likely that the observed large increase in viscosity (Figure 2) arises from the sphere-to-prolate ellipsoidal transition of the block copolymer micelles.

The increasing formation of the micellar clusters in the copolymer solutions with an increase in temperature on approaching their cloud points due to the presence of attractive intermicellar interaction is evident from Figure 6. The 20% copolymer solution becomes increasingly turbid on approaching the cloud point, and that is reflected in a progressive change in the nature of the correlation function plot. The presence of the slower moving micellar clusters becomes more and more prominent with an increase in the turbidity of the copolymer solution. An analysis of the data based on the stretched biexponential equation (eq 6) shows that  $A_s$  and  $\tau_s$ , i.e., the amplitudes and the relaxation time for the slow relaxation mode, respectively, increase significantly with an increase in the turbidity of the copolymer solution (Figure 6). This reflects an increasing degree of the presence and the size of the clusters as the copolymer solution approaches the cloud point.

To throw further light on the role of growth and interaction of the copolymer micelles in controlling the viscosity of the copolymer solutions in the presence of NaOH, we have studied the variation of the relative viscosity of the copolymer solution as a function of micellar volume fraction in the absence and presence of 1.1 M NaOH (Figure 7). Like in the case of DLS measurements, the viscosities of the copolymer solutions were measured at 2° below the cloud point. It can be seen that the NaOH induced increase in the viscosity is insignificant in the low concentration region and becomes more and more prominent as the concentration of the copolymer increases. To understand the effect of the attractive interaction in the observed viscosity enhancement, a comparison of the experimentally obtained plot at 1.1 M NaOH is made with those generated theoretically based on the adhesive





**Figure 8.** (a) Correlation function diagrams of 5% Pluronic P84 solutions recorded at 30 °C and 130° scattering angle as a function of NaOH concentration. The solid lines represent fits to the data. (b) The hydrodynamic radius of the micelles in 5% P84 solutions and the relative viscosity of the 5% P84 solution as a function of NaOH concentration at 30 °C.

hard sphere model. The calculations were carried out at two different attractive potential ( $\Omega$ ) and stickiness parameter ( $\tau^{-1}$ ) values based on the fractional surface layer thickness ( $\varepsilon$ ) value of 0.01. The two values of  $\Omega$  and  $\tau^{-1}$  at which the relative viscosity plots were generated separately were chosen to match with experimentally observed relative viscosities at the low and high micellar volume fractions, respectively. It is observed that the calculated and experimentally obtained viscosities could not be matched at the whole range of data points collected based on a single value of  $\Omega$  or  $\tau^{-1}$ . At a high value of  $\tau^{-1}$ , with high attractive interaction potential, the calculated value matches the experimentally observed one at 0.05 volume fraction, but it failed to do so at low volume fraction with the calculated value being significantly higher. The opposite is true in the case of the plot generated at a significantly lower value of  $\tau^{-1}$ , as the matching is found to be good at low micellar volume fraction only. These observations thus suggest that a sphere-to-rod micellar growth of the micelles as conjectured from the DLS studies is responsible for the observed viscosity enhancement in the aqueous copolymer solutions. The absence of any significant increase in the viscosity of the copolymer solution at low micellar volume fraction (1%) could result because of the fact that the micellar growth is not sizable enough to induce any viscosity change at low copolymer concentration.

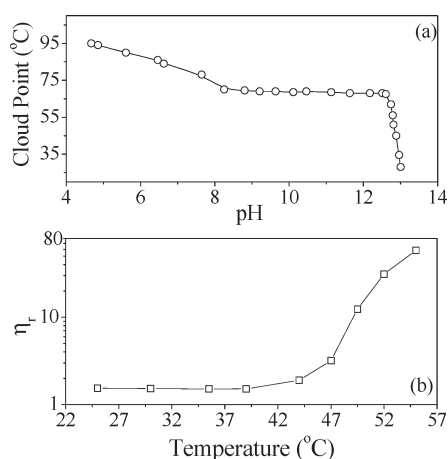
Finally, to understand whether the onset of the attractive intermicellar interaction and micellar shape transition in the aqueous T904 solution in the presence of NaOH are influenced by the change in pH or by the dehydrating effects of its constituent ions, we have also studied the effect of NaOH on the micellar solutions of Pluronic P84. Pluronic P84 has the same weight fraction of the PEO block (40%) as that of T904, but it does not show any pH sensitivity due to the absence of the central amine group. Quite interestingly, we observed that the P84 micelles too undergo a room temperature sphere-to-rod shape transition in the presence of NaOH, which is reflected from the DLS and viscosity data shown in Figure 8. A large shift in the correlation function data to higher time scale with an increase in the NaOH concentration, as shown in Figure 8a, is suggestive of the occurrence of the growth of the P84 micelles in the presence of NaOH. Like in the case of T904, the growth of

the micelles is also accompanied by a change in the nature of the correlation from single exponential to biexponential. The biexponential plots were fitted based on the stretched biexponential equation shown earlier as eq 6.

The evolutions of the size of the P84 micelles obtained from the analysis of the correlation function data and the relative viscosity of the P84 micellar solution as a function of NaOH concentration are shown in the Figure 8b. A large increase in the relative viscosity of the copolymer solution concomitant with the growth of the micelles is suggestive of the occurrence of a sphere-to-rod micellar shape change in the presence of NaOH. The enhancement in the viscosity starts occurring at higher NaOH concentration only after a significant growth of the micelles. P84 micelles are known to show a sphere-to-rod micellar shape transition on approaching the cloud point of the aqueous P84 solution. Like in the case of other Pluronics,<sup>21,30</sup> the salts like NaCl bring down the sphere-to-rod shape transition temperature of the P84 micelles due to their dehydrating effect on the copolymer molecules.<sup>60</sup> Detailed studies on the effects of different salts on the micellar aggregation characteristics suggest that the anions play a major role in dehydrating the copolymer molecules compared to the corresponding cations.<sup>61</sup> In the present case too, the dehydrating effect on the copolymer molecules in the presence of NaOH is likely to be determined by the  $\text{OH}^-$  ions with the  $\text{Na}^+$  ion playing a minor role. Though the dehydrating effects of the  $\text{OH}^-$  ion are not reported yet, the results shown in Figure 8 suggest that it brings down the sphere-to-rod shape transition temperature to induce a room temperature sphere-to-rod micellar growth. In fact, a comparison of the results shown in ref 60 with the results shown in Figure 8 suggests that the  $\text{OH}^-$  ion has a stronger dehydrating effect on the P84 micelles than the  $\text{Cl}^-$  ions.

The similarity of the above results with those observed in the case of T904 suggests that the onset of sphere-to-rod micellar growth and the attractive intermicellar interaction in the aqueous T904 solutions are influenced by the progressive dehydration of the T904 micelles with increase in the NaOH concentration. These results thus suggest that NaOH plays a dual role in enhancing the hydrophobicity and consequently in changing the aggregation characteristics of the T904 micelles. At low concentrations, it stabilizes the copolymer micelles by removing the protonated forms of the Tetronic molecules, and then at higher concentrations, it helps them to undergo micellar growth due to the dehydrating effect of the  $\text{OH}^-$  ion on these copolymer molecules. The variation of the cloud point (CP) of the 5% T904 solution with pH shown in Figure 9a illustrates this quite amply. As shown in the figure, the CP decreases up to a pH of about 8.25 and then remains constant up to a pH of about 12.5. Deprotonation of the copolymer molecules and the subsequent increase in their overall hydrophobicity with an increase in pH is responsible for the observed drop in CP up to pH 8.25. The existence of the plateau region up to about pH 12.5 after the initial drop in CP suggests that no significant deprotonation or dehydration of the copolymer occurs in the presence of NaOH in this pH region. A sharp drop in CP beyond pH 12.5 can be attributed to the dehydrating effect of NaOH on the copolymer molecules. The effect of deprotonation on the CP in the low pH region was earlier shown by Kadam et al.,<sup>46</sup> and the results shown in Figure 9a add the dehydrating effect of NaOH on CP to that observation. They have also shown that the salts like  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and NaCl, that are known to have strong dehydrating effects on the copolymer molecules, also lead to a decrease in the





**Figure 9.** (a) Cloud point of 5% T904 solution as a function of pH. (b) Relative viscosity of 5% T904 solution with 0.5 M NaOH on approaching the cloud point.

cloud point of the 5% T904 solution. Besides, a marginal but systematic increase in the viscosity of the copolymer solution is also observed in the presence of these salts on approaching their cloud points, due to a spherical-to-ellipsoidal micellar shape change.<sup>46</sup> To see whether a similar increase in the viscosity of the copolymer solution is induced in the presence of NaOH as a function of temperature consequent upon a micellar shape change, we have studied the viscosity of the 5% T904 solution from room temperature up to its cloud point in the presence of 0.5 M NaOH (Figure 9b). Unlike what has been observed in the case of salts,<sup>46</sup> where the increment in viscosity was only marginal, about a 40-fold increase in the viscosity of the copolymer solution is observed on approaching the CP of the 5% copolymer solution. This suggests that NaOH is significantly more effective in inducing a micellar growth than other salts used by Kadam et al.<sup>46</sup> In the literature, a sphere-to-rod shape change of the PEO–PPO–PEO based Pluronic micelles with an increase in temperature or upon addition of salt has been suggested to occur when the micellar radius reaches its limiting value determined by an entropically unfavorable stretching of the PO block.<sup>62,63</sup> We suggest that the ability of NaOH to deprotonate the micellar core makes it more effective in inducing growth of Tetronic micelles than the salts with strong dehydrating effects.

## CONCLUSIONS

The effect of NaOH on the aggregation characteristics of the X-shaped polyethylene oxide (PEO)–polypropylene oxide (PPO) based copolymer, Tetronic 904, has been studied by dynamic light scattering (DLS), small angle neutron scattering (SANS), and viscometry methods. The micellar solutions of this copolymer show a large increase in viscosity in the presence of NaOH due to a sphere-to-rod growth of the copolymer micelles. The observed micellar growth has been found to be accompanied by the onset of an attractive intermicellar interaction, leading to the observations of critical scattering on approaching the cloud points of the copolymer solutions. A comparison of these results with those observed in the aqueous Pluronic P84 solutions suggests that NaOH plays a dual role in promoting the observed onset of growth and attractive interaction of the Tetronic micelles. On one hand, it stabilizes the micelles by removing the protonated forms of the Tetronic molecules, and on the other

hand, it induces a micellar growth and attractive interaction because of its dehydrating effects on these Tetronic molecules.

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