

Micellar Structure of an Ethylene Oxide–Propylene Oxide Block Copolymer: A Small-Angle Neutron Scattering Study

Nirmesh J. Jain,[†] V. K. Aswal,[‡] P. S. Goyal,[‡] and P. Bahadur^{*,†}

Department of Chemistry, South Gujarat University, Udhana Magdalla Road, Surat 395 007, India, and Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received: June 9, 1998

Micellar solutions of a highly hydrophilic ethylene oxide–propylene oxide triblock copolymer, pluronic F88 (EO₁₀₃PO₃₉EO₁₀₃), in aqueous solution are examined by small-angle neutron scattering (SANS) at different concentrations and temperatures and in the presence of different salts. At temperature less than 30 °C, F88 solution in water (5 wt %) showed unimers which are fully dissolved Gaussian chains. The unimer-to-micelle transition takes place when the temperature or concentration is increased. Added neutral salt favors micellization of the copolymer at lower concentration/temperature. At temperature close to ambient, block copolymer forms micelles that consist of a central core, presumably dominated by the propylene oxide blocks, surrounded by a corona of highly hydrated ethylene oxide subchains. SANS analysis shows that the size of hydrophobic core increases as a part of PEO adjacent to the PPO core loses water with increasing temperature or salt (KCl) concentration. The micellar volume fraction increases with increasing concentration of block copolymer. The salting out effect of different electrolytes on structure of micelles is in the order KCl > KBr > KI. The effect of temperature on micellar solutions in the presence of KCl is also examined. It has been observed that the effect of added salt on the structural phase behavior of block copolymer is analogous to that of temperature. In all the above study, micelles are found to be spherical.

Introduction

Block copolymers have structural analogies with surfactants in that they possess two different moieties within their molecule and thus form microdomains in solid state and micelles in selective solvents. Polyethylene oxide/polypropylene oxide/polyethylene oxide (PEO/PPO/PEO) triblock copolymers are typical polymeric nonionic surfactants. A wide range of these copolymeric surfactants can be made just by altering the EO/PO ratio rather than by using different hydrophobes; therefore, logistically these have great economic attraction for making materials with varying surfactant properties. These copolymers PEO/PPO/PEO are available under trade names like pluronics (BASF), synperonics (ICI), and poloxamers or generic names like EPE polyols and are available as flakes, liquids, and pastes.^{1–4}

PEO/PPO/PEO triblock copolymers form micelles in water with the core of the PPO block surrounded by the shell of hydrated PEO end blocks. It is now well established that these block copolymers associate into micellar aggregates of spherical, rodlike, or possibly layered forms, depending on the molecular design, concentration, and temperature.^{5–7} Mortensen recently reviewed the structural characteristics of aqueous solutions of PEO/PPO/PEO triblock copolymer and their self-associated assemblies.⁸ Micelles of well-defined spherical shape and size coexist with unimers over a relatively wide temperature/concentration range. The micellar volume fraction increases with increasing concentration or temperature. Micelles grow in size on increasing temperature and undergo sphere-to-rod transition at elevated temperatures. Brown et al.⁹ studied a series

of similarly structured PEO/PPO/PEO triblock copolymers with constant PPO block weight and different percentages of PEO end blocks using dynamic light scattering and dynamic mechanical measurements. They found that, for high PEO content polymer, the micellar form of aggregates is stable up to relatively high temperatures while those having the lowest PEO content form two-phase systems dominated by large clusters. The copolymers with intermediate contents of PEO form micellar aggregates over a limited temperature range.^{5,9–12} Hatton et al.¹² recently studied micellar structure of pluronic P85 (EO₂₅-PO₄₀EO₂₅) as a function of temperature and concentration in the unimer-to-micelle transition region (region of 10–15 °C above the critical micelle temperature, CMT) using small-angle neutron scattering (SANS). They found that micelle core water decreases from 60 to 10% with increasing temperature in this region, with a corresponding increase in the micelle aggregation number. The micelle core radius remains almost constant. The broad nature of the unimer-to-micelle transition region was attributed to the structural changes accompanied by the replacement of micellar core water by polymer molecules.

Moreover, there are several studies of the structural characteristics of micelles above the unimer-to-micelle transition region.^{5,11} Conventional methods such as dynamic light scattering (DLS) and time-resolved fluorescence quenching (TRFQ) are not found to be suitable for determination of aggregation number (N_{agg}) in these systems; DLS does not account for water content in the micelle, and TRFQ suffers from slow quenching.^{2,13–15} Small-angle neutron scattering has been employed successfully to probe the structure of micelles,¹⁶ mixed micelles,¹⁷ and PEO/PPO/PEO micelles.^{6,8,11}

There are very few reports, to date, describing the role of electrolyte on the micellization of block copolymer in aqueous solution.^{14,18,19} The effect of added electrolyte on the micellar

* Author to whom correspondence should be addressed.

[†] South Gujarat University.

[‡] Bhabha Atomic Research Center.

behavior of nonionic surfactants is often not remarkable, as observed for ionic surfactants where the counterion condensation onto the charged micelle surface diminishes the effective polar head repulsions, favoring micellization. However, the presence of added salt has been found to exert a marked influence on the aggregation pattern and gelation of EO/PO block copolymers. For example, very hydrophilic copolymers (with ~80% PEO and low PPO molecular weight) do not micellize in water, even at concentration as high as 5 wt %, but added salt drastically induces micellization at very low concentration.¹⁸

Moreover, in the past,^{20,21} it has been shown that block copolymer solutions exhibit an inverse solubility–temperature relationship and undergo phase separation at a temperature usually referred to as the cloud point (CP). The mechanism of clouding phenomenon in aqueous solutions of block copolymer has been highly debated in recent years,^{22–24} and several explanations are put forward to understand the micellar structure near the CP. The addition of salt decreases the CP of block copolymer and enables the study of micellar structure in aqueous block copolymeric solution close to the CP at low temperatures.

However, until now, no report has appeared on micellar structures of block copolymers in aqueous solutions in the presence of salt by SANS. This prompted us to take up the present work, in which we report SANS data on the hydrophilic block copolymer F88 (EO₁₀₃PO₃₉EO₁₀₃) in aqueous solution at different concentrations/temperatures with special reference to the presence of added salt. The role of different electrolytes on the structural phase behavior of micelles is studied. The aim of the present study is to examine the variation in micelle structure (size and shape) under various solution conditions.

Experimental Section

The pluronic PEO/PPO/PEO triblock copolymer F88 (EO₁₀₃–PO₃₉EO₁₀₃, MW = 11 400) was obtained from BASF Corp. (Parsippany, NJ) as a gift sample and was used as received. The inorganic salts were all AnalaR grade (BDH) chemicals.

The SANS experiments were carried out on micellar solutions of PEO/PPO/PEO triblock copolymer F88. All of the final solutions used for neutron-scattering measurements were prepared in D₂O (obtained from heavy water division of BARC, Mumbai, India, and at least 99.5 atom % pure). This provides a very good contrast between micelle and the solvent in a SANS experiment. Neutron-scattering measurements were performed on the 7.0-m (source-to-detector distance) SANS instrument at the CIRUS Reactor, (Trombay, India).²⁵ The sample-to-detector distance was 1.8 m for all runs. This spectrometer makes use of a BeO-filtered beam and has a resolution ($\Delta Q/Q$) of about 15% at $Q = 0.05 \text{ \AA}^{-1}$. The angular distribution of the scattered neutron is recorded using an indigenously built one-dimensional position-sensitive detector (PSD). The accessible wave transfer, $Q (= 4\pi \sin 0.5 \theta/\lambda$, where λ is the wavelength of the incident neutrons and θ is the scattering angle), range of this instrument is between 0.02 and 0.3 \AA^{-1} . The wavelength was 0.52 nm.

The solutions were held in 0.5-cm path length UV-grade quartz sample holders with tight-fitting Teflon stoppers, sealed with Parafilm. The effect of salt concentration (0–2 M KCl) on the SANS distribution was investigated on micellar solutions of 5 wt % pluronic F88. The effect of different kinds of salt (KCl, KBr, and KI) on the SANS profile of the copolymer was examined. The variation in neutron-scattering profile with increasing temperature at fixed concentration (5 wt %) of F88 and increasing concentration of the copolymer (at fixed temperature, 40 °C) was also studied. Furthermore, the effect of temperature on the scattering of neutrons was examined for

micellar systems of pluronic F88 in the presence of a fixed concentration of salt (1 M).

Scattering intensities from the copolymer solutions were corrected for detector background, empty cell scattering, and sample transmission. The resulting corrected intensities were normalized to absolute cross section units and thus a plot for $d\Sigma/d\Omega$ vs Q was obtained. This absolute calibration has an estimated uncertainty of 10%. The experimental points are fitted using a nonlinear least-squares routine as described below. Comparisons between the experimental and calculated cross sections are shown in Figures 1–6.

SANS Analysis

Calculation of the Scattering Intensity. For a monodisperse system of particles, the coherent differential scattering cross section, $d\Sigma/d\Omega$, derived by Hayter and Penfold,²⁶ and Chen,²⁷ can be written as

$$d\Sigma/d\Omega = n_m V_m^2 (\rho_m - \rho_s)^2 P(Q) S(Q) + B \quad (1)$$

The same expression for noninteracting micelles [i.e., $S(Q) \sim 1$] is given by

$$d\Sigma/d\Omega = n_m V_m^2 (\rho_m - \rho_s)^2 P(Q) + B$$

where n_m denotes the number density of the micelles of volume V_m , ρ_m and ρ_s are scattering length densities of the micelle and solvent, respectively, $P(Q)$ is the single-particle (intraparticle) structure factor, and $S(Q)$ is the interparticle structure factor. B is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample.

The pluronic micelles consist of a hydrophobic core of PPO surrounded by the hydrated shell of PEO. However, a part of PEO from the side of the PPO core becomes hydrophobic due to dehydration when the temperature is raised or salt is added. Thus, the micellar core not only consists of PPO but also includes a part of PEO that has become hydrophobic. For the SANS experiment, when the pluronic solutions are prepared in D₂O, there is very good contrast between the hydrophobic core and the solvent, while there is a very poor contrast between the hydrated shell and the solvent. As a result, $P(Q)$ depends only on the hydrophobic core radius. The $P(Q)$ for spherical micelles can be written as

$$P(Q) = \left[\left(\frac{3}{(QR_c)^3} \sin(QR_c) - QR_c \cos(QR_c) \right) \right]^2 \quad (2)$$

where R_c is the hydrophobic core radius which is attributed to the size of the micellar core.

Structure Factor for Interacting Micelles. The interparticle structure factor $S(Q)$ depends on the spatial distribution of micelles. As the temperature or the concentration is increased, the scattering function becomes dominated by a pronounced correlation peak, revealing significant micelle–micelle interaction. The structure factor, $S(Q)$, is given by the radial distribution function, $g(r)$, describing the arrangement of the micelles,²⁸

$$S(Q) = 1 + 4\pi n \int (g(r) - 1) \frac{\sin(Qr)}{QR} r^2 dr \quad (3)$$

Using the classical Ornstein–Zernike approximation for the spatial correlation fluctuations and the Percus–Yevick approximation for describing the direct correlation between two scattering objects²⁹ with a hard-sphere nearest-neighbor interact-

ing potential, the structure factor (eq 3) can be written in the analytical form^{5,30,31}

$$S(Q) = \frac{1}{1 + 24\phi G(2QR_{hs}, \phi)/(2QR_{hs})} \quad (4)$$

where R_{hs} , the hard-sphere radius, consisting of both PPO and PEO, and is the physical size of the micelle. ϕ is the hard-sphere volume fraction of the micelles in the solution.

G is a function of $x = 2qR_{hs}$ and ϕ :

$$\phi = \frac{C4\pi R_{hs}^3}{3N_{agg}} \quad (5)$$

where C is the concentration of pluronic solution in wt %.

$$G(x, \phi) = (\alpha(\phi)/x^2)[\sin x - x \cos x] + (\beta(\phi)/x^3)[2x \sin x + (2 - x^2)\cos x - 2] + (\gamma(\phi)/x^5)\{-x^4 \cos x + 4[(3x^2 - 6) \cos x + (x^3 - 6x) \sin x + 6]\}$$

where α , β , and γ are defined as

$$\begin{aligned} \alpha &= (1 + 2\phi)^2/(1 - \phi)^4 \\ \beta &= -6\phi(1 + \phi/2)^2/(1 - \phi)^4 \\ \gamma &= (\phi/2)(1 + 2\phi)^2/(1 - \phi)^4 \end{aligned}$$

Thus, in fitting experimental data from pluronic solutions to eq 1, there are three unknown parameters: R , R_{hs} , and ϕ .

The aggregation number can be obtained from the knowledge of core size.

$$N_{agg} = 4\pi(R_{c_{ppo}})^3/3nV_{PO} \quad (6)$$

where $n = 39$ is the number of propylene oxide monomers in the PPO block, $(R_{c_{ppo}})$ is the radius of the core due to PPO only, and V_{PO} is the volume of propylene oxide monomer.

The number of EO units (from each copolymer molecule) which lose water when the temperature or the salt concentration is increased has been calculated from the following equation:

$$n_{EO} = \frac{4\pi[R_c^3 - (R_{c_{ppo}})^3]}{3V_{EO}N_{agg}} \quad (7)$$

The number of water molecules (n_w) attached to each EO group of the copolymer molecule in the hydrated shell is

$$n_w = \frac{(4\pi/3)[R_{hs}^3 - R_c^3] - N_{agg}V_{EO}(2m - n_{EO})}{V_{D_2O}N_{agg}(2m - n_{EO})} \quad (8)$$

where $m = 103$ is the number of EO units in each PEO block of the copolymer molecule, and V_{EO} and V_{D_2O} are the volumes of an ethylene oxide monomer and a D_2O molecule, respectively.

Results and Discussion

Effect of Temperature. The SANS data (Figure 1) show a scattering function for 5 wt % aqueous solution of F88 obtained at 30 °C. The scattering function shows a relatively weak q dependence and only small intensities. Such a behavior is because F88, being a highly hydrophilic polymer (containing 80% of PEO), does not micellize in water, even up to 5 wt %

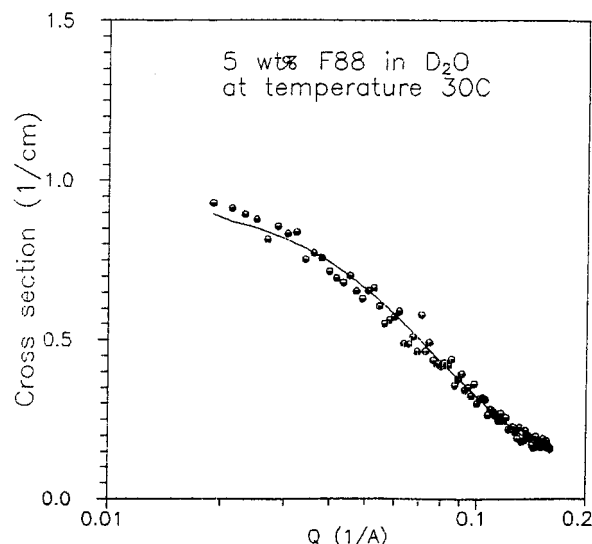


Figure 1. Scattering curve for F88 unimer in D_2O at 30 °C. The lines shown are theoretical fits, and the solid marks are experimentally determined data points.

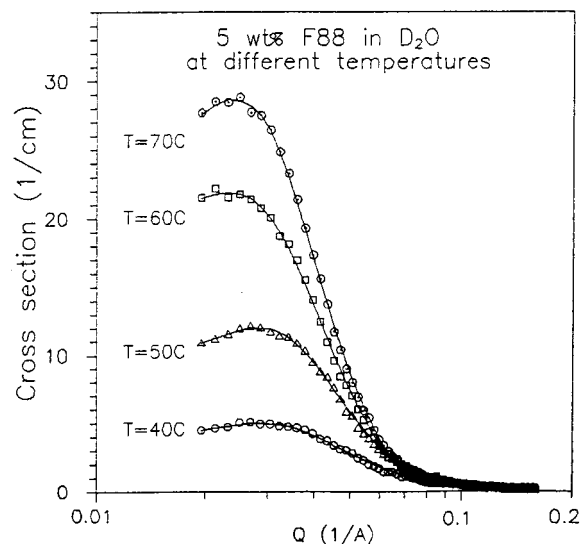


Figure 2. Scattering curves for 5 wt % F88 in D_2O at different temperatures.

concentration of copolymer.³² The critical micellar temperature (cmt) for a 5 wt % solution of F88 as reported by Hatton et al.³² is 31°C. At temperatures lower than 30 °C, a 5 wt % aqueous solution of block copolymer F88 appears as independent, fully dissolved Gaussian copolymer molecules.⁹ The scattering function is accordingly in good agreement with that of a randomly distributed coil, following the Debye function,

$$d\Sigma/d\Omega \approx (-1 + x + e^{-x})x^{-2} \quad (9)$$

where $x = (QR_g)^2$, R_g being the polymer radius of gyration. The scattering function at 30 °C gives the radius of gyration, $R_g = 21$ Å. A hydrodynamic radius of 29 Å has been reported for F88 unimers, determined using dynamic light scattering, by Brown et al.⁹

The SANS data from 5 wt % F88 solutions at different temperatures ($T = 40, 50, 60$, and 70 °C) are shown in Figure 2. At temperatures higher than the cmt, the micelles are in thermodynamic equilibrium with the unimers. Although both micellar aggregates and unimers are present in the solution at every temperature examined here, the measured scattering

TABLE 1: Effect of Temperature on 5 wt % F88^a

(a)			
temp (°C)	R_c (Å)	R_{hs} (Å)	ϕ
40	38	84	0.08
50	44	85	0.09
60	50	88	0.09
70	52	87	0.09
(b)			
temp (°C)	N_{agg}	n_w	
40	62	3.40	
50	96	1.30	
60	141	0.14	
70	158	0.01	
(c)			
temp (°C)	n_{EO}	n_w	
40	0	3.5	
50	28	4.3	
60	65	6.5	
70	80	6.8	

^a At $T = 30$ °C, solution contains only unimers having radius of gyration about 21 Å.

function at a given temperature is dominated by the large aggregates because the scattering function of an object is proportional to the squared volume. However, intermicellar correlation becomes the dominant component in the scattering function at higher temperatures.

As can be seen from Figure 2, a sharp correlation peak is observed in SANS distributions. Generally, this correlation peak, arising due to interparticle structure factor $S(Q)$, is seen at $Q_m \approx 2\pi/d$, where d is the distance between two micelles. No shift in the position of the correlation peak is observed here; therefore, there is no change in the number density of micelles. This accounts for the constant value of hard-sphere volume fraction for these measurements (Table 1a). However, an increase in neutron-scattering intensity (Figure 2) is due to an increase in the size of the PPO core and not an increase in the number density of micelles.

The micellar parameters obtained from SANS analysis are given in Table 1. It can be seen that the hard-sphere radius ($R_{hs} \approx 85$ – 90 Å) for micellar solutions of F88 is independent of temperature range (40– 70 °C). The micellar core radius (R_c) progressively increases with temperature, while the hard-sphere volume fraction (ϕ) remains almost constant. These results are similar to what has been observed in the past by Mortensen et al.,^{5,7,11} who have extensively studied such systems through different techniques, including SANS. They have explained the above results, assuming that PPO molecules in the hydrophobic core undergo a conformational change with changes in temperature and/or concentration. On the basis of this assumption, the aggregation number (N_{agg}) and the number of water molecules associated with each EO unit (n_w) at different temperatures are calculated and are shown in Table 1b. The N_{agg} increases from 62 at 40 °C to 158 at 70 °C, while n_w shows an opposite trend; i.e., n_w decreases from 3.4 water molecules at 40 °C to 0.01 (i.e., almost no water in PEO shell) at 70 °C. However, an increase in the micellar core radius (or N_{agg}) and a decrease in n_w is attributed to enhanced hydrophobicity of the PPO block due to dehydration of the PEO shell at higher temperatures. Dehydration of the PEO shell at elevated temperatures decreases its volume. The constant value of hard-sphere radius over the entire temperature range (40– 70 °C) studied in the experiment is explained as due to the additive

effects of two opposite phenomena: (i) increase in the size of PPO core and (ii) decrease in the volume of PEO shell at elevated temperatures. However, this explanation, based on the model given in earlier references, does not appear to be consistent with the following facts.

(1) If the aggregation number (N_{agg}) increases, the hard-sphere volume fraction (ϕ) should decrease as the R_{hs} is remaining same. However, to the contrary, an almost constant value of ϕ (0.09) is observed here.

(2) At higher temperatures, n_w is decreasing greatly; therefore, the contrast between PEO and the solvent should be just as significant as that between PPO and the solvent. Consequently, the difference between R_c and R_{hs} should be negligible. However, SANS analysis gives very distinct values of R_c and R_{hs} .

(3) At higher temperature ($T = 70$ °C), the small value of n_w ($=0.01$) suggests that there is almost no water in the PEO shell. The PEO shell is no longer hydrophilic enough to keep micelles in the soluble state in water, and ultimately the system should lead to phase separation. However, measurements show that block copolymeric solutions of F88 are transparent even up to 95 °C.

Thus, in order to explain the above-mentioned results, it seems that assumption of a conformational change of PPO in the hydrophobic core is not sufficient. We assume that a part of PEO from the side of PPO is becoming hydrophobic when the temperature is raised. R_c now consists of PPO and that part of PEO which has been dehydrated. Such EO units have been determined using eq 7 and are shown in Table 1c. This assumption is now consistent with the following facts.

(1) There is an increase in the core radius of micelles with increasing temperature, and this is quite self-explanatory with the model proposed by us.

(2) While the value of aggregation number for 5 wt % F88 in its aqueous solution at 40 °C is found to be 62, a constant value of aggregation number (i.e., $N_{agg} = 62$) is observed at higher temperatures. This is contradictory to earlier reports^{5,7} on N_{agg} with increasing temperature. Aggregation number ($N_{agg} = 62$) is calculated using eq 6, where $(R_c)_{PPO}$ is taken as equal to R_c of the micelle at 40 °C. Up to 40 °C when the volume fraction of micelles is about to saturate, we assume that the effect of temperature only helps to increase the volume fraction of micelles (unimer-to-micelle transition) and that water is dehydrated from the PPO core only and not from EO units of the hydrated PEO shell. Similar results have also been reported by Hatton et al.,¹² where it has been shown that, in the unimer-to-micelle transition region, PPO core water decreases from 60 to 10%. An increase in N_{agg} is expected in the temperature range of 30 – 40 °C; however, this region could not be extensively studied. Such a study has been reported in ref 12 where an increase in N_{agg} with temperature is observed in this region. Besides, a constant value of N_{agg} at temperatures higher than 40 °C can be explained from the constant values of micellar volume fraction (ϕ) and R_{hs} .

(3) The increase in the number of EO units which lose water from hydrated PEO shell is attributed to an enhanced degree of dehydration at elevated temperatures. These dehydrated water molecules are displaced toward the outer surface of PEO shell but remain within the shell. Consequently, number of water molecules associated per EO unit (n_w) increases. Hence, an increase in the size of hydrophobic core with a decrease in the hydrated volume of the PEO shell is observed. This accounts for the constant value of the hard-sphere radius with increasing temperature.

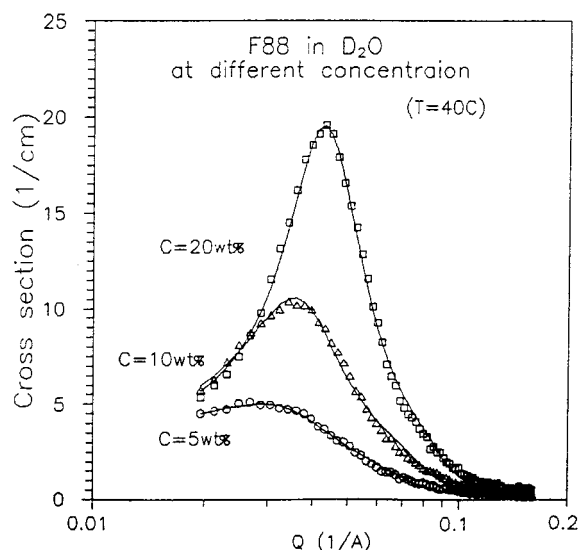


Figure 3. Scattering curves at 40 °C for F88 in D₂O at different concentrations.

TABLE 2: Effect of Concentration of F88 at 40 °C

concentration (wt %)	R_c (Å)	R_{hs} (Å)	ϕ	n_w
5	38	84	0.08	3.5
10	38	81	0.17	2.8
20	37	80	0.36	3.1

(4) As can be seen from Table 1c, up to 70 °C, only 80 EO units are dehydrated, while there are still 136 hydrated EO units in each copolymer in the PEO shell, thereby maintaining sufficient hydrophilicity and imparting a good hydrophilic–lipophilic balance between the hydrophobic core and the hydrophilic PEO shell. Thus, micelles are quite stable, even at higher temperatures, and this accounts for the transparent nature of the system and explains why the system does not phase-separate up to 70 °C. However, if the system is taken at very high temperatures, ($T > 100$ °C), it is quite possible that n_{EO} might be very large, while the number of EO units containing water in hydrated the PEO shell would be much smaller, thus disturbing the hydrophilic–lipophilic balance, leading to phase separation. Thus, the model is consistent with the high CP value of F88 block copolymer.

(5) At every temperature, a hydrated PEO shell having a sufficient amount of water accounts for a very good contrast between hydrophobic core–solvent and a poor contrast for hydrated PEO shell–solvent; thus, quite distinct values of R_c and R_{hs} appear reasonable.

Effect of F88 Concentration. In Figure 3, SANS distributions as a function of copolymer concentrations ($C = 5, 10, 20$ wt %) at 40 °C are shown. As already indicated, the correlation peak in $d\Sigma/d\Omega$ occurs at $Q_m \approx 2\pi/d$, where d is the average distance between micelles. With an increase in the concentration, the interparticle distance decreases, and thus the peak shifts to higher Q values. It is seen that calculated distributions give the peak positions in $d\Sigma/d\Omega$ with a good correspondence with experimentally determined points. As the copolymer concentration increases, it is found that the peak in the measured distribution sharpens with significant shifts in peak position. Shifting of the correlation peak to high Q values indicates an increase in the number density of micelles. This increasing number density of micelles is probably responsible for the observed increase in the hard-sphere volume fraction. It is observed from Table 2, that R_c , R_{hs} , and n_w are independent of any variation in copolymer concentration. This can be argued

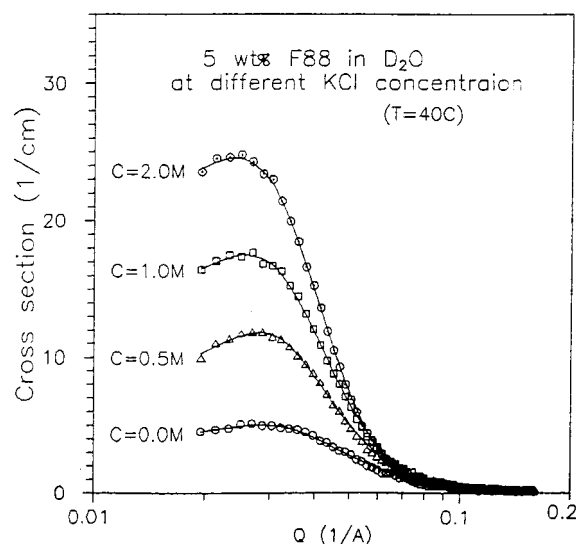


Figure 4. Scattering curves for 5 wt % F88 in D₂O at different concentrations of KCl at 40 °C.

TABLE 3: Effect of Salt KCl on 5 wt % F88 at 40 °C

[KCl] M	R_c (Å)	R_{hs} (Å)	ϕ	n_{EO}	n_w
0.0	38	84	0.08	0	3.5
0.5	45	87	0.09	34	5.0
1.0	48	87	0.09	52	5.6
2.0	52	87	0.09	80	6.8

from the fact that an increase in the copolymer concentration does not alter the characteristics of the PEO or PPO block in its molecule, and hence, constant value of these parameters can be expected. Also, an increase in the scattering intensity (Figure 3) with increasing concentration of copolymer may be attributed to the increase in the volume fraction or number density of micelles with increasing concentration. Similar observations for EO/PO copolymers have been made in the past by Mortensen et al.^{5,11}

Effect of Salt. Effects of salt concentrations on SANS distributions are shown in Figure 4. Scattering curves shown are for a 5 wt % solution of copolymer F88 at varying salt concentrations ($C = 0, 0.5, 1.0, 2.0$ M) at 40 °C. Scattering functions show that, as the salt concentration increases, the intensity increases and the Q dependence becomes stronger. Since Q_m is found to be independent of salt concentration, it can be concluded that the number density of micelles remains unaltered with increasing salt concentration. Now, there being no change in the number density of micelles upon addition of salt (0–2 M), a constant value of hard-sphere volume fraction (Table 3) can be expected. Addition of KCl dehydrates the PEO shell by its “salting out” action,²⁰ similar to the effect of temperature, and induces hydrophobicity in the PPO block of the copolymer molecule. Here also, it is assumed that addition of salt dehydrates water first from that portion of PEO which is adjacent to PPO core of the micelle. This accounts for the observed increase in core radius of the micelle. Moreover, constant value of R_{hs} and the increasing trend of n_{EO} and n_w in all measurements could be explained as in the earlier case of temperature effect on SANS distribution. The increasing trend in the differential cross section with increasing salt concentration is due to progressive increases in core radius.

Effect of Temperature at Fixed Salt Concentration. The effect of temperature on SANS distribution for 5 wt % solutions of F88 at a fixed concentration of KCl (2 M) is shown in Figure 5. These measurements were carried out to investigate the structural phase behavior of micelles close to the cloud point

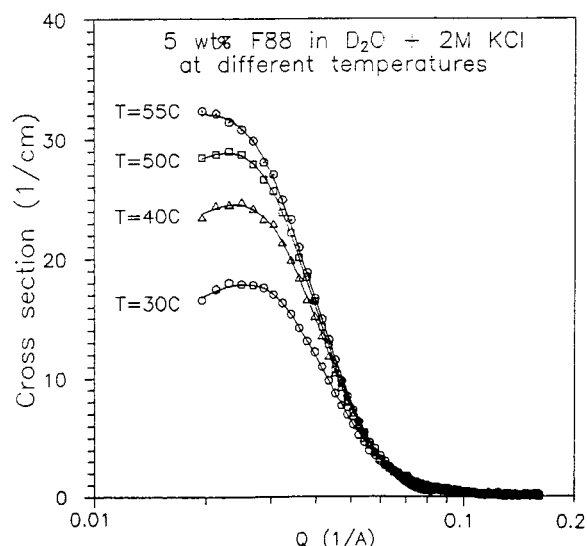


Figure 5. Scattering curves for 5 wt % F88 in D₂O in the presence of 2 M KCl at different temperatures.

TABLE 4: Effect of Temperature on 5 wt % F88 + 2 M KCl

temp °C	R_c (Å)	R_{hs} (Å)	ϕ	n_{EO}	n_w
30	49	84	0.08	58	5.8
40	52	87	0.09	80	6.8
50	54	87	0.09	95	7.7
55	55	88	0.09	103	8.8

of block copolymer. A 5 wt % solution of F88 has a CP value of about 60 °C in the presence of 2 M KCl. Here, trends in the scattered intensity are found similar to those observed in the case of increasing temperature in the absence of salt. There is no shift in the peak position of scattering curves; hence, there is no change in the number density of micelles and there is a constant value of micellar volume fraction (Table 4), as per speculation. In the presence of 2 M KCl at 55 °C (CP = 60 °C), the F88 scattering function give a good fit using the hard-sphere model. This suggests that micelles retain the same basic structure (spherical), even at temperatures close to the CP. This is also supported by dynamic light scattering studies.^{9,33} However, Mortensen et al.⁷ have shown that, in a solution of F88 in water, a spherical-to-prolate transition may occur at temperatures close to 90–95 °C (CP \approx 100 °C), while at temperatures lower than this, micelles are spherical. Trends in other parameters, such as R_c , R_{hs} , n_{EO} , and n_w , are similar to those observed in the case of temperature and salt effects on the system.

Effect of Different Types of Salts. The effect of different types of salts, viz., KCl, KBr, and KI (1 M), on the SANS distribution is shown in Figure 6. Scattering curves indicate that the effect of these inorganic salts on scattering intensity is in the order KCl > KBr > KI. While variation of salts has no effect on the peak position of scattering curves, a constant value of micellar volume fraction/number density of micelles is as expected. It can be seen from Table 5 that the maximum values of R_c , n_{EO} , and n_w are observed in the case of KCl over other salts. This is because of a stronger dehydrating action of Cl⁻ ion than the other anions due to its highest electronegativity and smallest size. The almost constant value of R_{hs} is explained as in the case of salt/temperature effect

Conclusions. Solutions of highly hydrophilic block copolymer F88 under various solution conditions (i.e., temperature, salt, concentration) obtained using small-angle neutron scattering reveal that, at low temperatures, unimers are fully dissolved

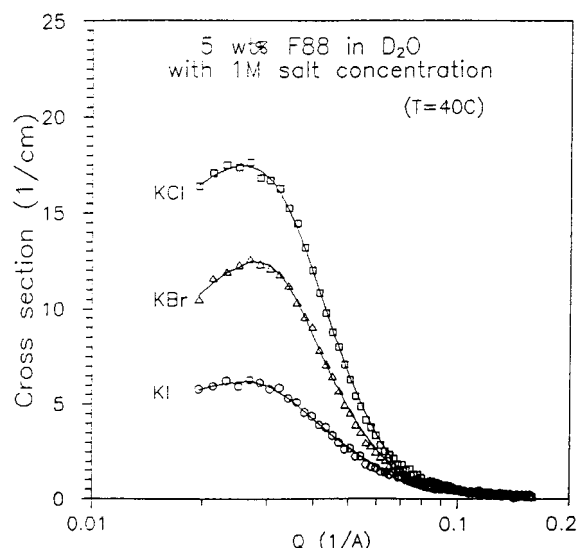


Figure 6. Scattering curves for 5 wt % F88 in D₂O in the presence of different salts (1 M).

TABLE 5: Comparative Effect of Different Salts (1 M) on 5 wt % F88

salt	R_c (Å)	R_{hs} (Å)	ϕ	n_{EO}	n_w
KCl	48	84	0.08	52	5.6
KBr	46	87	0.09	40	5.2
KI	42	88	0.09	18	4.8

Gaussian chains with radius of gyration of about 21 Å. Micelles continue to be spherical up to the phase separation. The hard-sphere radius of micelles ($R_{hs} \approx 85$ –90 Å) is almost independent of any variation in solution condition. The core radius of micelles progressively increases with increasing temperature/salt concentration. An increase in the core radius is attributed to the dehydration of PEO shell, remaining adjacent to PPO core. Micellar volume fraction increases with increasing concentration but remains almost constant with varying temperature/salt concentration. Aggregation number ($N_{agg} = 62$) does not increase with concentration/temperature/salt concentration. The effect of salt is found to be parallel to that of temperature. Among inorganic salts, KCl exerts the strongest effect.²⁰

Acknowledgment. We thank the Department of Atomic Energy for financial support of this work (Grant no. IUC/PB-54). We also thank Dr. B. A. Dasannacharya for his interest in this work.

References and Notes

- (1) Bahadur, P.; Riess, G. *Tenside, Surfactants, Deterg.* **1991**, 28, 173.
- (2) Almgren, M.; Brown, W.; Hvidt, S. *Colloid Polym. Sci.* **1995**, 273, 2.
- (3) Alexandridis, P.; Hatton, T. A. *Colloids Surf. A* **1995**, 96, 1.
- (4) Chu, B.; Zhou, Z. *Surf. Sci. Ser.* **1996**, 60, 67.
- (5) Mortensen, K.; Pedersen, J. S. *Macromolecules* **1993**, 26, 805.
- (6) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, 27, 4145.
- (7) Mortensen, K.; Brown, W. *Macromolecules* **1993**, 26, 4128.
- (8) Mortensen, K. *J. Phys. Condens. Matter* **1996**, 8, A103.
- (9) Brown, W.; Schillen, K.; Hvidt, S. *J. Phys. Chem.* **1992**, 96, 6038.
- (10) Mortensen, K. *Europhys. Lett.* **1992**, 19, 599.
- (11) Mortensen, K.; Talmon, Y. *Macromolecules* **1995**, 28, 8829.
- (12) Hatton, T. A.; Goldmints, I.; Gottberg, F. K. V.; Smith, K. A. *Langmuir* **1997**, 13, 3659.
- (13) Almgren, M.; Van Stam, J.; Lindblad, C.; Li, P.; Stilbs, P.; Bahadur, P. *J. Phys. Chem* **1991**, 95, 5677.
- (14) Almgren, M.; Alsins, J.; Bahadur, P. *Langmuir* **1991**, 7, 446.

- (15) Nivaggioli, T.; Alexandridis, P.; Hatton, T. A.; Yekta, A.; Winnik, M. A. *Langmuir* **1995**, *11*, 730.
- (16) (a) Zana, R. *Surfactant Solutions: New Methods of Investigation*; Marcel Dekker, Inc.: New York, 1987. (b) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. *J. Phys. Chem* **1996**, *100*, 11664.
- (17) (a) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. *J. Phys. Chem.* **1997**, *101*, 5639. (b) Penfold, J.; Staples, E.; Tucker, I. *Adv. Colloid Interface Sci.* **1996**, *68*, 31.
- (18) Bahadur, P.; Li, P.; Almgren, M.; Brown, W. *Langmuir* **1992**, *8*, 1903.
- (19) Attwood, D.; Collett, J. H.; Tait, C. J. *Int. J. Pharm.* **1985**, *26*, 25.
- (20) Pandya, K.; Lad, K.; Bahadur, P. *J. Macromol. Sci.* **1993**, *A30* (1), 1.
- (21) Bahadur, P.; Pandya, K.; Almgren, M.; Li, P.; Stilbs, P. *Colloid Polym. Sci.* **1993**, *271*, 657.
- (22) Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2053.
- (23) Goldstein, R. E. *J. Chem. Phys.* **1984**, *89*, 5340.
- (24) Karlstrom, G. *J. Phys. Chem* **1985**, *89*, 4962.
- (25) Goyal, P. S.; Aswal, V. K.; Joshi, J. V. Bhabha Atomic Research Centre Report No. BARC/1995/I/018; Bhabha Atomic Research Center: Surat, India, 1995.
- (26) (a) Hayter, J. B.; Penfold, J. *Colloid Polym. Sci.* **1983**, *261*, 1022. (b) Hayter, J. B.; Penfold, J. *Mol. Phys.* **1981**, *42*, 109. (c) Hansen, J. P.; Hayter, J. B. *Mol. Phys.* **1982**, *46*, 109. (d) Hayter, J. B.; Penfold, J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1851.
- (27) (a) Chen, S. H. *Annu. Rev. Phys. Chem* **1986**, *37*, 351. (b) Chen, S.H.; Lin, T. L. *Methods of Experimental Physics*; Academic Press: New York, 1987; Vol. 23B, p 489.
- (28) Guinier, A.; Fournet, G. *Small Angle Scattering of X-Rays*; Wiley: New York, 1955.
- (29) Percus, J. K.; Yevick, G. *J. Phys. Rev.* **1958**, *110*, 1.
- (30) Ashcroft, N. W.; Leckner, J. *Phys. Rev.* **1966**, *145*, 83.
- (31) Kinnig, D. J.; Thomas, E. L. *Macromolecules* **1984**, *17*, 1712.
- (32) Alexandridis, P.; Holtzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2414.
- (33) Brown, W.; Schillen, K.; Almgren, M.; Hvidt, S. *J. Phys. Chem* **1991**, *95*, 1850.