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Physicochemical Properties of PEO-PPO-PEO Triblock Copolymer (Mol.Wt. 2000) Micelles in Sodium Dodecyl Sulfate (SDS) Micellar Environment

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Abstract — The hydration of the polymer micelles has been directly determined from the measurements of conductance of micellar solutions of the triblock copolymer (PEO-PPO-PEO) in 25 mM SDS (fixed) and in 5 mM NaCl (fixed), using the principle of the obstruction of electrolyte migration by the polymer. The asymmetry of the micellar entities of the polymer and the polymer-SDS mixed micellar systems and their average axial ratios are calculated using the intrinsic viscosity and hydration data obeying Simha-Einstein equation. The hydration of the polymer has also been determined by Einstein and Vand equations, and good agreement with the conductivity results obtained. Hydration number and micellar sizes are found to be variable with temperature. The aggregation number, $\overline{N}$ of the polymer in an aqueous solution of SDS (25 mM, fixed) was determined by fluorescence spectroscopic technique considering the SDS solution as the solvent only in one case, and in the other case, the micellar concentration of SDS had been taken into account to consider the SDS-polymer mixed system. Both $\overline{N}$ and the Stern-Volmer constant (K_{sv}) are variable with temperature. The shape of the polymer micelles has been observed to be ellipsoidal rather than spherical. From the absolute values of the axes, the micellar volume, hydrodynamic radius, radius of gyration, diffusional coefficients as well as translational (τ_D), rotational (τ_r) and effective (τ_a) correlation times have been calculated. The partial molal volume of the polymer micelles has also been determined and its comparison with the molar volume of the pure polymer suggested a volume contraction due to the immobilization of the water phase by the hydrophilic head groups of the polymer. The thermodynamic activation parameters for the viscous flow favour a more ordered water structure around the polymer micelles at higher temperatures.

Keywords : *Geometry of the micelles, Triblock copolymer, Mixed micelles, Aggregation, Cor-*

relation times and Thermodynamic parameters.

INTRODUCTION

Self-assembling of surfactants in aqueous solutions is a fascinating recent area of research. The hydrophobic interactions provide the driving force for the aggregation of the surfactants into micelles, liquid crystalline phases and reverse micelles in the presence of water or mixed solvents. Poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymers of varying molecular weights are commercially available nonionic polymeric surfactants due to two dissimilar moieties, i.e., hydrophilic PEO block and hydrophobic PPO block within the same molecule and their micellization in aqueous solution and adsorption on to interfaces resemble those of nonionic surfactants. The micellization of amphiphilic block copolymers is inherently more complex than that of conventional low molecular weight surfactants. PEO-PPO-PEO triblock copolymers have been the subject of a wide variety of recent publications. This is due to their importance in practical applications as detergents, stabilizers, emulsifiers, cosmetics, drug release, treatment of burns, water purification, etc [1,2]. Moreover, their low toxicity is essential for medical applications such as drug solubilization and controlled release. Furthermore, block copolymers offer great potential in creating tailor-made supramolecules because of wider variations in the molecular architecture compared to small detergent molecules.

Despite their long-time use, many aspects of their solution behavior remain obscure, stimulating a large number of studies reported in the literature. Among some of the topics studied so far, one could be enlightened on their aggregation in aqueous and water/organic solvents mixtures [3,4], the determination of their phase diagram [5,6], their adsorption on to solid surfaces, drug delivery [7,8] and the formation of aqueous biphasic systems for bio-separations [9]. The block copolymers, made by BASF ("Pluronics") and ICI ("Poloxamers") are also available as triblocks PPO-PEO-PPO ("Reverse Pluronics") or in dendrimer architecture with PEO-PPO or PPO-PEO segments linked to an ethylene diamine core.

Because of the incompatibility of the two blocks of amphiphilic copolymers, they form micellar aggregates in selective solvents. Unlike pure surfactant systems, where a variety of structures (spherical, cylindrical, wormlike micelles, etc.) are well known, block copolymer micelles are commonly reported to have a spherical shape. For block copolymers containing a polyelectrolyte as the hydrophobic block, non-spherical aggregates have been observed in aqueous solutions and the shape of these micelles can be influenced by the ionic strength of the solvent. For non-ionic block copolymers, the shape transformation induced by the addition of nonionic surfactants was reported in a Cryo-TEM study [10]. The incorporation of cosurfactants in surfactant micelles changes the natural curvature of the surfactant film, which can cause a transformation of the overall micellar structure and thus allow tuning of the micellar shape. The diblock copolymer, poly (butadiene)-poly (ethylene oxide), PB-PEO with a ratio of the block sizes $N_{PB}/N_{PEO} > 3/4$, forms worm like micelles in aqueous solutions [11,12]. A number of PEO-PPO-PEO triblock copolymers dissolved in aqueous media have been shown to aggregate with increasing temperature in the form of micelles [4,13,14], having a core presumably dominated by PPO and a surface corona dominated by hydrated PEO segments [15].

The most characteristic property of the pluronic diols is the inverse temperature dependence of the critical micelle concentration (cmc) i.e., the cmc decreases as the temperature increases [4,16]. Interesting rheological properties follow, and gel phases are formed in some Pluronics with increase in temperature, due to the growth of the micelles and interpenetration of their coronas. This behaviour has been successfully modelled by Karlstrom *et al.*, Linse and Hurter *et al.* based on the analysis of the chain conformations expected for polymers containing the $-CH_2CH_2O-$ group [17-21].

Micellization [22], microviscosity [23] of pluronic PEO-PPO-PEO block copolymer solutions and the temperature effects [24] on the structural properties of pluronic P_{104} and F_{108} PEO-PPO-PEO block copolymer solutions have been studied extensively by Alexandridis *et al.* Desai *et al.* have reported the effect of additives on the micellization of PEO-PPO-PEO block copolymer F127 in aqueous solution [25]. The micelle formation, aggregation, hydration, shape, size, correlation times and some thermodynamic properties of water-soluble methoxy poly (ethylene glycol) macromonomer and macromonomer based graft-copolymer and homopolymers have been studied by us earlier using various techniques [26, 27]. Self-diffusion [both by cyclic voltammetry (CV) and Fourier transform pulsed gradient spin echo (FTPGSE) NMR], molecular dynamics and film forming ability (i.e., monolayer characteristics) studies had been made by us in the recent past [28-33] on the above macromonomer and macromonomer based polymers in absence and presence of SDS micelles at various temperatures as functions of mole compositions and field frequency dispersions using NMR spin-lattice relaxation time measurements and Langmuir film balance techniques.

In the present investigation, we have determined the size, shape and hydration of the micelles composed of the triblock copolymer based on the molecular weight, transport, conductance and hydrodynamic measurements [27, 34, 35]. As the polymer is insoluble in water because of the high content of PPO as hydrophobic groups, the polymer has been solubilized in SDS micelles to study the various physicochemical properties of these micelles. Recently, we have reported the critical micelle concentration and aggregation number of the water insoluble polymer-2800 in SDS micellar environment using conductivity, fluorescence and surface tensiometric techniques [36]. Self-diffusion studies on the above polymer-2800 in aqueous SDS micelles and vice versa were made using cyclic voltammetric and dynamic light scattering techniques [37].

EXPERIMENTAL

Materials : Polymer-2000, i.e., poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymer of molecular weight 2000, viz., $E_4P_{28}E_4$ was obtained from Aldrich and used without further purification. Here, E = Ethylene oxide = OCH_2CH_2, P = propylene oxide = $OCH_2CH (CH_3)$, and the subscripts denote the number-average block lengths in the chain units. This triblock copolymer contained 85% poly (propylene oxide) by weight and is insoluble in water. Sodium Dodecyl Sulfate (SDS) was obtained from Aldrich, recrystallized twice from 95% ethanol, rinsed with ethanol and anhydrous ether at 0°C and dried under vacuum for 90 h. Pyrene and *N*-cetylpyridinium chloride (CPC) were obtained from Fluka and recrystallized twice from spectroscopic grade ethanol. The characteristics of the pyrene, SDS and CPC used in this study were described earlier [38-43]. All the other reagents used in this study were of analytical grades. Doubly distilled water of specific conductance 2–3 $\mu S\ cm^{-1}$ at 25 °C was used as a solvent medium throughout the experiment.

Methods : *Conductance measurements* — The conductance measurements were taken in a Global digital conductivity meter Model No. DCM 900, made in India. A dip type cell of cell constant 1.0 cm^{-1} was used. The uncertainty in the conductance measurement was within ± 0.4%.

Fluorescence Spectroscopy — Fluorescence spectroscopic technique was used to study the micelle formation in the aqueous medium. Fluorescence spectroscopic measurements were made on a Hitachi Model No. 650-40 Fluorimeter with the temperature of the cell maintained by a thermostat (accuracy ± 0.1°C). For the determination of the aggregation number of the micelles, pyrene was used as an external probe (1×10^{-6} M, fixed) and CPC as the quencher. Different solutions containing fixed polymer-2000 and 25 mM SDS were prepared with quencher concentrations varying from 0.5×10^{-4} to 3×10^{-4} M. The ratio between the molar concentrations of pyrene and micellar concentrations was kept at $<<1$ so that the question of perturbation of the micellar structure by the probe would not arise at all. The fluorescence emission measurements were carried out at 372, 378, 385 and 392 nm upon excitation at 320 nm; the aggregation number, $\bar{N}$ for the polymer-SDS mixed micellar system (where the contribution of SDS micelles was also taken into account), polymeric micelles in SDS (aqueous SDS micellar solution was considered as solvent only) and SDS in water were determined at various temperatures. The details regarding sample preparations, precautions and fluorescence measurements (both steady state and time resolved methods) are described in earlier and recent publications [44-47].

Viscosity and Density Measurements — The viscosities of different concentrations of the polymer-2000 in 25 mM SDS were measured by an Ostwald viscometer at various temperatures. The viscometer was calibrated using 10% and 20% sucrose solutions in water. The results are in good agreement with the values available in the literature. The viscometer gives a flow time 240 s for water at 25 °C. The temperatures of measurements were accurate within ±0.05 °C. Uncertainties in temperature, density measurements and flow detection imparted a maximum error of ± 0.7% to the measured viscosity. Densities of the solutions were measured in a calibrated pycnometer. The details regarding viscosity and density measurements have been described earlier [34,35,42,43]. Solutions having different concentrations of the polymer were prepared. A definite volume (3 ml) of each individual solution was then taken in a dried viscometer whose time of flow was measured at least three times after being allowed to come to thermal equilibrium. The densities of the corresponding solutions were also measured under identical environmental conditions. The measured values were accurate within ± 0.4%.

RESULTS AND DISCUSSION

To assess the validity of the following conductivity equation, a plot of (k'/k) vs $(k'/k)C$ is shown in Fig.1.

$$(k'/k) = 1 - 1.93\, V_h\, (k'/k).C \tag{1}$$

where, k' and k are the specific conductances of NaCl solutions in presence and absence of obstructant (here, polymer), respectively. V_h and C are the hydrated specific volume and concentration of the obstructant, respectively. The deviations are observed in the experimental points beyond the concentration 0.04 g/ml of the polymer, which is at par with the earlier observations on various systems [27,34,35,48]. The viscosity data have been variously plotted to advantage in Fig. 2, 3 and 4. The hydrated specific volume V_h, intrinsic viscosity $[\eta]$, Huggins constant K, shape factor ν, hydration factor δ (g of water bound/g of surfactant), axial ratio

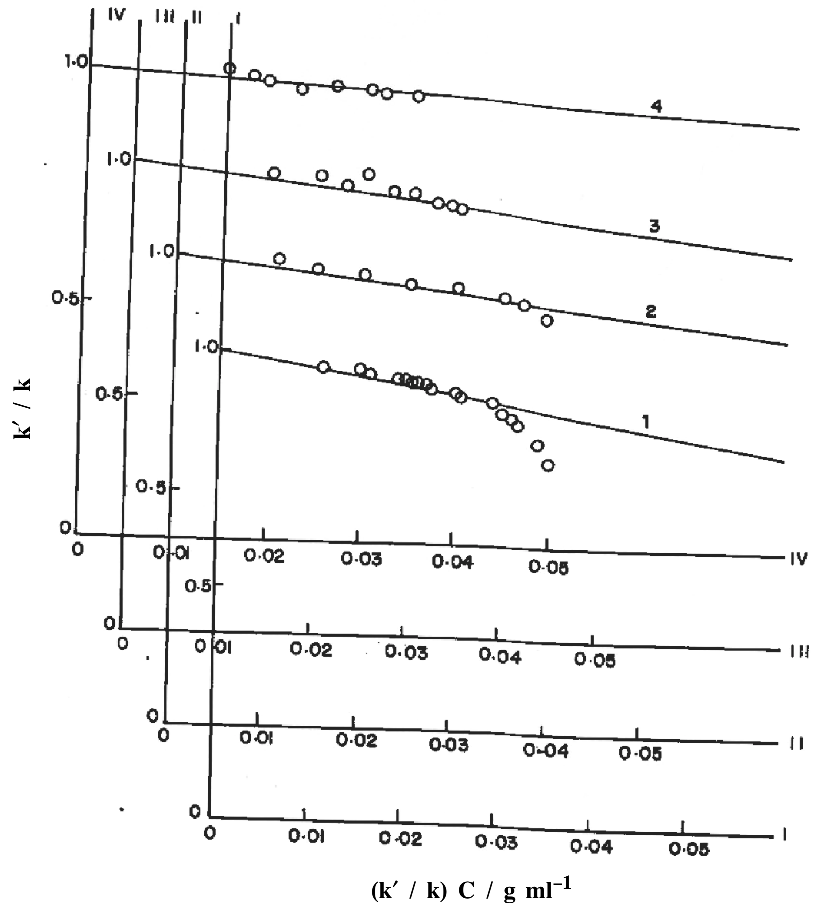

Fig. 1. Plot of (k′/k) vs (k′/k).C. Application of conductivity equation (1) to [Polymer-SDS] micellar systems at various temperatures using 5 mM NaCl (fixed) and 25 mM SDS (fixed) solutions. Curves 1, 2, 3 and 4 are at temperatures 25°, 35°, 45° and 50°C, respectively.

(a/b), total micellar volume M_v, hydrodynamic radius R_h, radius of gyration R_G, diffusion coefficient D, partial molal volume v, excess volume V^E, correlation times, τ, etc. of the polymeric micelles in SDS (25 mM aqueous SDS micellar solution was considered as reference) and polymer-SDS mixed micellar system (where the contribution of SDS micelles was also taken into account) have been estimated as described earlier [27,34,35]. The calculated ν from Vand's equation agree with the intrinsic viscosity derived value (Simha-Einstein equation) [34,35]. The [η], K, ν obtained are given in Table 1 and V_h, δ and hydration numbers obtained from Einstein, Vand and conductivity equations are presented in Table 2. The diffusional and dimensional properties of the polymeric micelles in 25 mM SDS (where SDS micellar solution was considered as reference only) and polymer-SDS mixed micellar systems at different temperatures are given in Tables 3 and 4, respectively. These include the axial ratio, the lengths of semimajor and semiminor axes, hydrodynamic radius, radius of gyration, radius for equivalent sphere (R_0), frictional coefficients (f/f_0) for hydrated and unhydrated states and diffusion coefficients, etc. at different temperatures.

Micellar volume and various correlation times of polymer micelles in SDS

TABLE 1

Intrinsic viscosity, Huggins's constant, Particle asymmetry of Polymer-2000 – SDS (25 mM) micelles at different temperatures.

T (°C)	[η] ml/g	K	ν from Simha – Einstein equation	ν at δ = 0
25	17.0	0.17	9.84	17.10
35	6.2	0.86	5.39	6.20
45	7.6	0.70	6.95	7.58
50	9.2	0.63	8.88	9.20

TABLE 2

Hydrated specific volume, bound water and hydration number of Polymer-2000 – SDS (25 mM) micelles at different temperatures.

T (°C)	V_h (ml/g)			δ (g/g)			Hydration Number		
	Einst.	Cond.	Vand	Einst.	Cond.	Vand	Einst.	Cond.	Vand
25	1.75	1.73	1.75	0.75	0.73	0.73	81.21	83.75	84.34
35	1.17	1.15	1.16	0.17	0.15	0.16	17.34	18.88	18.60
45	1.12	1.09	1.10	0.12	0.09	0.10	9.90	12.87	11.17
50	1.05	1.04	1.05	0.04	0.04	0.04	3.40	4.94	5.33

TABLE 3

Diffusional and dimensional properties of Polymer-2000 micelles in 25 mM SDS (as solvent) at different temperatures for (A) prolate and (B) oblate shaped models.

T (°C)	*Axial* ratio	a (Å)	b (Å)	R_h (Å)	R_G (Å)	R_0 (Å)	f/f_0 (hydrated)	f/f_o (unhydrated)	$D/10^{-6}$ (cm^2 s^{-1})
(A) PROLATE									
25	17.40	4.96	86.30	56.48	54.63	33.30	1.70	1.88	0.49
35	11.50	5.64	64.84	43.55	41.08	28.73	1.51	1.62	0.68
45	13.80	4.78	65.95	43.91	41.77	27.49	1.59	1.73	0.81
50	16.31	4.14	67.51	44.62	42.74	26.63	1.67	1.84	0.90
(B) OBLATE									
25	13.83	79.94	5.78	53.20	50.62	33.30	1.59	1.52	0.52
35	7.30	55.73	7.63	38.49	35.41	28.73	1.34	1.24	0.77
45	9.61	58.43	6.08	39.58	37.05	27.49	1.44	1.36	0.90
50	12.40	61.63	4.97	40.98	39.04	26.63	1.54	1.47	0.98

TABLE 4

Diffusional and dimensional properties of Polymer-2000 – SDS (25 mM) mixed micelles at different temperatures for (A) prolate and (B) oblate shaped models.

T (°C)	Axial ratio	a (Å)	b (Å)	R_h (Å)	R_G (Å)	R_0 (Å)	f/f_0 (hydrated)	f/f_o (unhydrated)	$D/10^{-6}$ (cm^2 s^{-1})
(A) PROLATE									
25	17.40	8.33	144.98	95.62	91.77	55.95	1.70	1.88	0.30
35	11.51	9.46	108.85	73.04	68.98	48.22	1.51	1.62	0.41
45	13.80	8.15	112.45	74.86	71.21	46.88	1.59	1.73	0.48
50	16.31	7.12	116.11	76.74	73.50	45.79	1.67	1.84	0.52
(B) OBLATE									
25	18.83	134.30	9.71	89.39	85.05	55.95	1.59	1.53	0.32
35	7.30	93.55	12.81	64.63	59.44	48.22	1.34	1.24	0.46
45	9.60	99.63	10.38	67.58	63.19	46.88	1.44	1.36	0.53
50	2.40	105.99	8.55	70.92	67.14	45.79	1.54	1.47	0.56

solvent and polymer-SDS mixed micellar systems at various temperatures are given in Tables 5 and 6, respectively. The Stern-Volmer constant (K_{sv}) and aggregation numbers ($\bar{N}$) for the above systems were determined by fluorescence methods [44-47] using Stern-Volmer and Turro-Yekta plots, respectively. The graphical representations of these plots are not shown. However, these data are also given in Tables 5 and 6. Partial molal volumes v, molar volume V and excess volume V^E of the micelles determined from density measurements are also given in Table 7. The recorded v is the mean of at least five values, which have been observed to be practically independent of the polymer-SDS concentrations above the cmc. The thermodynamic activation parameters for viscous flow of the aqueous polymer-SDS solutions were calculated from Eyring's equation [49]. These values are depicted in Table 8. The plot of log η_{poly} vs. 1/T has been shown in Fig. 5.

Knowing the hydration of the micelles, the shape factor, ν can be found. On

TABLE 5

Micellar volume, Aggregation number, Stern-Volmer constant and various correlation times of the Polymer-2000 micelles in 25 mM SDS (as reference) at different temperatures.

T (°C)	M_V /10^{-24} (ℓ)	Aggregation number	$K_{SV}/10^4$ (ℓ.mol^{-1})	τ_r (ns)	τ_D (ns)	τ_a (ns)
25	154.67	27	1.25	29.45	22.09	12.62
35	99.25	26	1.00	17.70	13.27	7.58
45	87.00	24	0.80	12.96	9.7	5.55
50	79.03	23	0.70	10.49	7.87	4.50

TABLE 6

Micellar volume, Aggregation number, Stern-Volmer constant and various Correlation times of the Polymer-2000-SDS (25mM) mixed micelles at different temperatures

T (°C)	M_V /10^{-24} (ℓ)	Aggregation number	$K_{SV}/10^4$ (ℓ.mol^{-1})	τ_r (ns)	τ_D (ns)	τ_a (ns)
25	733.20	128	3.75	139.62	104.72	59.84
35	469.57	123	3.20	83.85	62.89	35.94
45	431.39	119	2.70	64.25	48.19	27.54
50	402.03	117	2.20	53.34	40.01	22.86

TABLE 7

Partial Molal Volume (ν), Molar Volume (V), and Excess Volume (V^E) of Polymer-2000 – SDS (25 mM, fixed) micelles at different temperatures.

T	ν	V	V^E
(°C)	(ml /mol)	(ml /mol)	(ml /mol)
25	1955.60	1988.07	–32.47
35	1959.93	1988.00	–38.07
45	1967.12	2006.02	–38.90
50	1971.44	2010.05	–38.61

TABLE 8

Thermodynamic activation parameters for viscous flow of polymer-2000 micelles in 25 mM SDS at 25°C.

[Polymer]	DG*	ΔH*	ΔS*
(M)	(kJ mol^{-1})	(kJ mol^{-1})	(J K^{-1} mol^{-1})
0.000	9.25	14.93	19.06
0.005	9.28	12.19	9.83
0.010	9.60	13.33	12.52
0.015	9.93	15.68	19.31
0.020	10.25	17.98	25.93
0.030	10.77	20.93	34.10

an average this hydration number has been observed to be 82, 18, 10 and 4 at 25°, 35°, 45° and 50°C, respectively. At temperatures higher than 25°C, the intrinsic viscosity was decreased. It is due to decreased hydration. However, above 35°C, the change in [η] is not significant. The shape was changed towards more asymmetry (probably oblate ellipsoids). However, at temperatures 35°C and above, the asymmetry has been reduced. The reasonable low values of [η] have spoken in favour of oblate or prolate ellipsoids of polymer micelles, and the direct evaluation of hydration has enabled to estimate the micellar geometry of the polymer. At 25°C and above, the Huggins constant is less than 2.0 indicating that the shape of polymer-SDS micelles is not spherical irrespective of temperature (Table 1). Therefore, prolate and oblate ellipsoidal models are also equally possible to consider for the determination of the

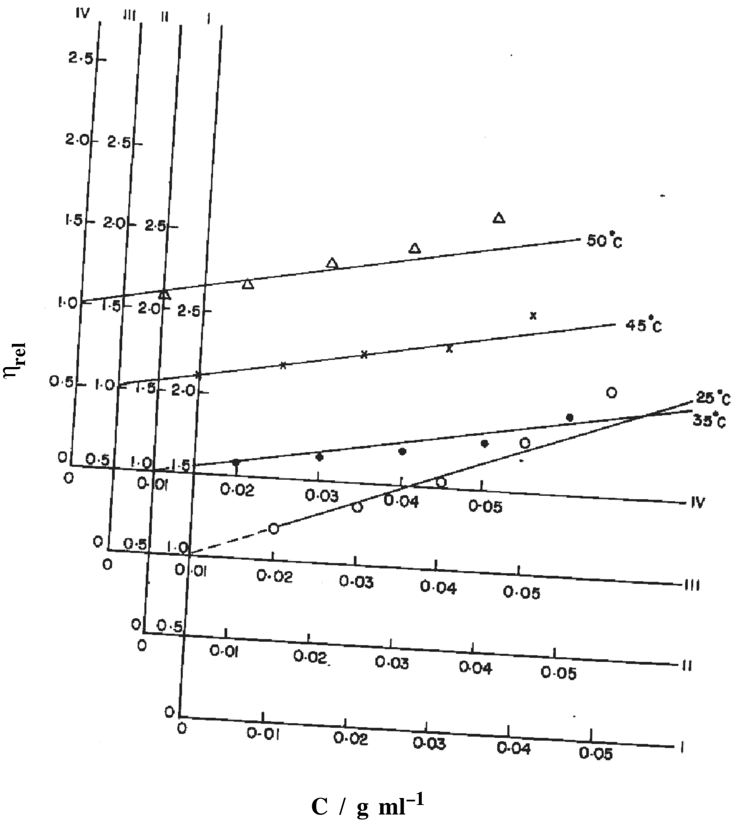

Fig. 2. Plot of η_{rel} vs C (concentration of the polymer) at 25°, 35°, 45° and 50°C in the presence of fixed concentrations of SDS (25 mM). Concentrations of the polymer are 0.01, 0.02, 0.03, 0.04 and 0.05 g/ml, respectively. Curves 1, 2, 3 and 4 are at temperatures 25°, 35°, 45° and 50°C, respectively.

geometry. *K* has steadily increased with temperature up to 35°C and afterwards decreased, indicating that the medium has tended to become a poor solvent.

The molecular asymmetry and hydration at different temperatures as observed in Tables 1 and 2 have revealed that the dimensions change with temperature. The amount of PEO in triblock copolymer is approximately 15%, which is considered to be hydrophilic. The number of poly (oxy ethylene) chain is thus 8. On the consideration that it has a meandering conformation (the length of each oxy ethylene

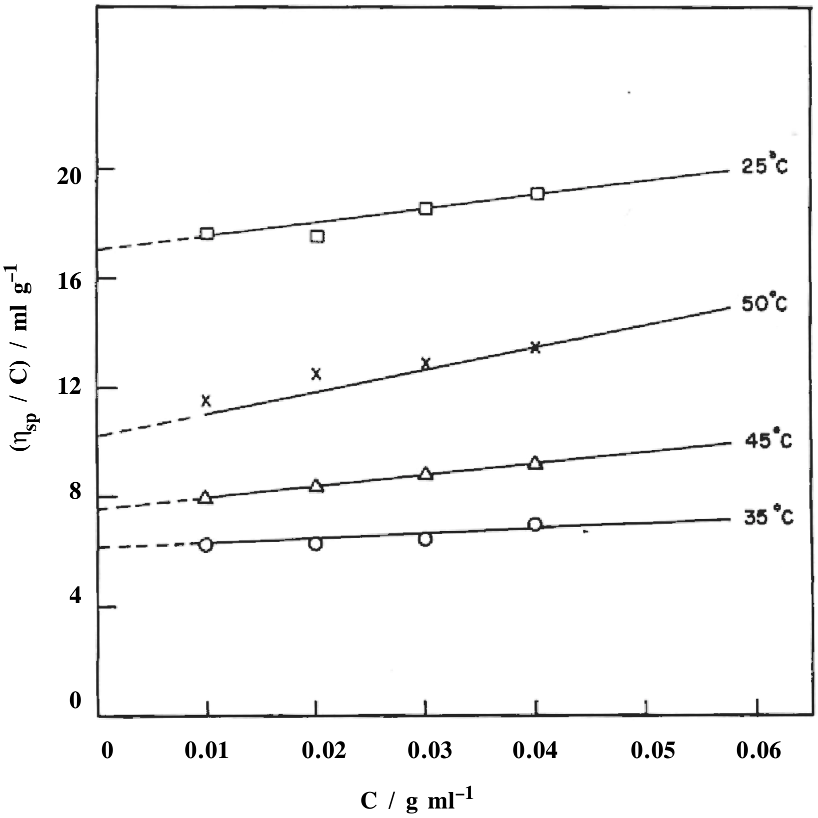

Fig. 3. Plot of η_{sp}/C vs C (concentration of the polymer) at 25°, 35°, 45° and 50°C in the presence of fixed concentrations of SDS (25 mM). The polymer concentrations varied (0.01, 0.02, 0.03 and 0.04 g/ml.

unit is 1.8Å), the hydrophilic contribution is, therefore, 14.4 Å. Considering the oblate model, the semimajor axis is thus 79.94 Å with 65.54 Å attributed to the hydrophobic part at 25°C [see Table 3 (B)]. Keeping the hydrophobic part 65.54 Å constant with temperatures, then at higher temperature the length of the head group is remarkably low. At 35°, 45° and 50°C, they are only the negative values of 9.8, 7.8 and 3.9 Å, respectively. Therefore, a great degree of coiling of the POE chain (head group of the polymer) and contraction of the PPO hydrophobic chain have been envisaged [cf. Table 3 (B)]. The total micellar contrtibution is 79.94 Å with 65.54 Å and 14.4 Å contributed by the hydrophobic and hydrophilic poly (ethylene oxide) head groups, respectively. However, at 35°C, the interaction with water makes 20%

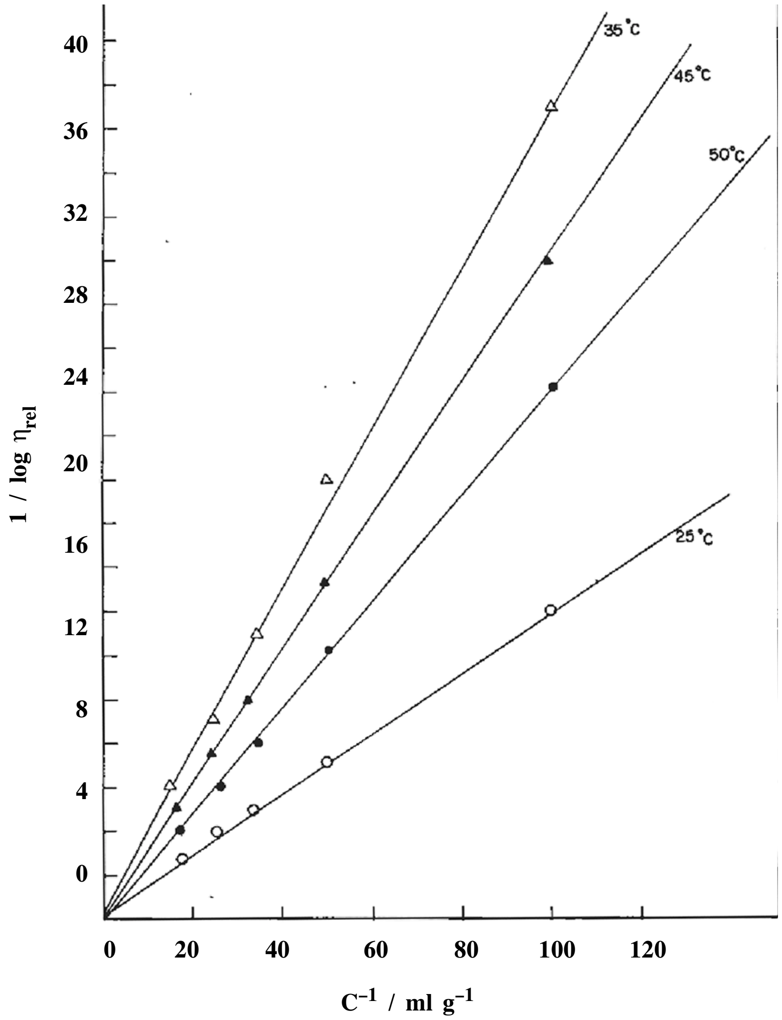

Fig. 4. Plot of (1/log η_{rel}) vs (1/C) at 25°, 35°, 45° and 50°C in the presence of fixed concentrations of SDS (25 mM). Concentrations of the polymer are 0.01, 0.02, 0.03, 0.04 and 0.05 g/ml, respectively.

reduction of hydrophobic chain length of the polymer towards semimajor axis, whereas 80% reduction of hydrophilic chain length has been observed towards semimajor axis. The chain (random coil or meander) has collapsed at higher temperature through loss of water. According to Dennis *et al.* [50], the semimajor axis remains invariant with temperature. If this is the fact, then prolate model [cf. Table 3 (A)] is likely to be possible. If 65.54 and 14.4 Å are attributed to hydrophobic and hydrophilic contribution respectively, then the chain may be extended to random coil considering semiminor axis of the prolate model [cf. Table 3 (A)] at 25°C.

Based on the intrinsic viscosity and aggregation number [27], the hydrodynamic radius of the equivalent sphere (R_0) for the polymer and polymer – SDS mixed micellar systems have been estimated without taking hydration into account using the following equation (2) :

$$R_0 = \{3[\eta]\, M_w/(10\,\pi\, N_A)\}^{1/3} \tag{2}$$

where M_w and N_A are the weight average molecular weight of the micelles and Avogadro's number, respectively. The R_0 values of the $E_4P_{28}E_4$ triblock copolymer (mol.wt.2000) in unhydrated state were found to be 53, 37, 39 and 41 Å at 25, 35, 45 and 50°C, respectively. However, when hydration has been taken into account, the R_0 values of the above polymer [cf. Table 3] decreased to 33, 29, 28 and 27 Å at 25, 35, 45 and 50°C, respectively. The reduction of the size of the polymer is due to its binding in SDS micelles. In the same analogy, the R_0 values of the polymer-SDS mixed micellar system in unhydrated state were found to be 88, 63, 66 and 70 Å at 25, 35, 45 and 50°C, respectively and decreased to 56, 48, 47 and 46 Å at 25, 35, 45 and 50°C, respectively when hydration has been taken into account. At low temperatures, the hydration of the polymer results in lesser steric repulsion between the head groups leading to larger micelles.

Above cmc, the partial molal volume at a particular temperature remains almost constant; addition of micelles cannot cause expansion or contraction of the aqueous medium. As the excess volume V^E is negative, some kind of organization of water molecules by the POE chain around the micelles has been revealed. Hydrogen bonding of water through such chains can be a very common occurrence. In the present polymeric micelles in SDS solutions, each oxygen centre of the poly (oxyethylene) groups has fixed on the average roughly 10, 2.5, 1.5 and 0.5 water molecules at 25, 35, 45 and 50°C, respectively (cf. Table 2). At 25°C, each oxygen centre of Triton X-100, macromonomer, Tween-20 and Tween-80 micelles bind on an average 1.4, 5.2, 1.4 and 0.7 water molecules, respectively [27,34,35].

Considering hydrated oblate spheroid, (f/f_0) has been observed to vary as $(a/b)^{0.18\text{-}0.15}$. Oblate spheroids normally show a variation of $(a/b)^{0.33}$; for hydrated prolate spheroids (f/f_0) has been observed to vary as $(b/a)^{0.19\text{-}0.16}$. Considering the unhydrated

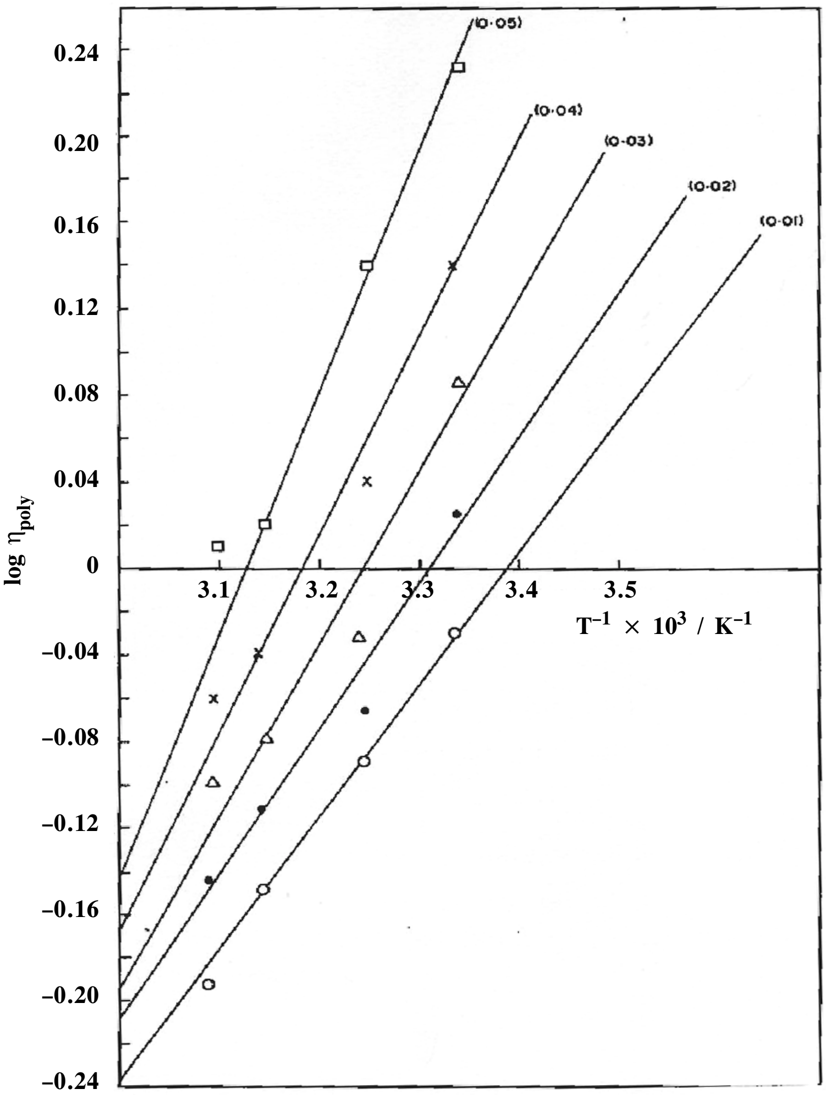

Fig. 5. Eyring's plot of log η_{poly} vs (1/T) for the polymer-2000 micelles for various concentrations of polymer (0.01, 0.02, 0.03, 0.04 and 0.05 g/ml) in 25 mM SDS environment.

oblate spheroids, (f/f_0) vary as $(a/b)^{0.16\text{-}0.11}$ and for unhydrated prolate spheroids the variation is $(b/a)^{0.22\text{-}0.20}$. These variations are the same for the polymer-SDS mixed micellar systems.

The increased microviscosity of the environment is also possible in the presence of the polymer in SDS micelles. ΔH^* was found to be 20.9 kJ mol^{-1} at higher concentration of the polymer, viz., 0.03 M (cf. Table-8), obtained from viscosity measurements. It is interesting to note that all the correlation time values are maximum at 25°C. However, there is a significant change of τ_r, τ_D and τ_a values of the polymer micelles in SDS above 25°C (i.e., from 35 to 50°C). These values are on an average 13.7, 10.3 and 5.8 ns, respectively (cf. Table 5). However, they were decreased drastically with temperature above 25°C. The same trend has also been observed in polymer-SDS mixed micellar system (cf. Table 6).

Although for polymer-SDS micellar systems, the partial molal volume increases with increase in temperature, the excess volume V^E is more negative at higher temperatures (V^E is less negative at temperature 25°C) (cf. Table 7). This is in contrast to the behaviour exhibited by both Tween-20 and Tween-80 polymeric micelles. The dissimilarity in the molecular structure of the Triton X-100, macromonomer, Tweens and polymer may account for the difference [27,34,35]. Although the hydrophilic contribution in the polymer is more or less the same as in the Triton X-100, the hydrophobic contribution (due to propylene oxide, PPO) is dramatically more than those of Triton X-100 and other surfactants. Therefore, polymer micelles have lower degree of hydration at higher temperatures, which is not useful for the preparation of water-soluble polymers. Because of this reason, the solubilization of the present polymer was made by using SDS micelles (i.e., SDS micellar solution acts as a solvent)

Thermodynamic activation parameters for viscous flow indicates ordered micellar environment for the polymer-SDS system. Both ΔH^* and ΔS^* have higher magnitudes in the presence of the polymer-SDS micelles than in its absence (Table-8). ΔH^* and ΔS^* values show a very good compensation between them. A single line embracing five surfactant points including polymer-SDS to similar structural environment for all of them, has been obtained with a compensation temperature 25°C (see Fig.6).

CONCLUSION

The geometry of the polymer-2000 micelles in SDS micelles was determined using independent knowledge of micellar hydration [27,34,35]. The shape of the polymer micelles has been observed to be ellipsoidal rather than spherical. The aggregation number and Stern-Volmer constant of the polymer micelles as well as SDS-polymer mixed micelles are found to be variable with temperature and they are maximum at

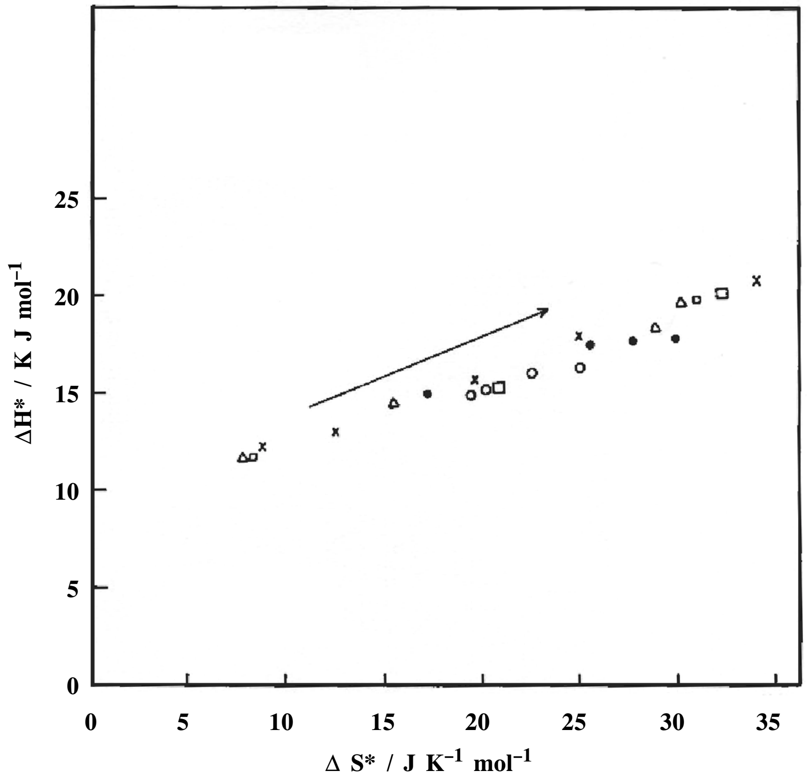

Fig. 6. Enthalpy (ΔH*) vs entropy (ΔS*) compensation plot for polymer-2000 at 25°C and at different concentrations of the surfactants (concentrations of the surfactants are 0.02, 0.04, 0.06 and 0.08; concentrations of the polymer are 0.005, 0.010, 0.015, 0.020 and 0.030 M, respectively). The arrow indicates the concentrations of the surfactants and polymer are in the direction from lower to higher concentrations. o Macromonomer, • Triton X 100, Δ Tween-20, □ Tween-80, × Polymer-2000.

25°C indicating that the polymer micelles attained a state of fully extended conformation at 25°C although hydration number decreased with increase in temperature. The partial molal volume of the polymer micelles has also been determined and its comparison with the molar volume of the pure polymer suggested a volume contraction due to immobilization of the water phase by the hydrophilic head groups of the polymer. The thermodynamic activation parameters for viscous flow favor a more ordered structure at higher temperatures. Organization of water molecules by the poly (ethylene oxide) chain around the polymer micelles in SDS has been revealed by showing negative V^E values. The geometry of the polymer micelles individually and also in mixed state with SDS micelles are determined and the results suggest that a prolate model is more probable, if semimajor axis remains invariant with temperature [50]. The diffusion coefficients of the polymer and polymer-SDS mixed micelles increase with temperature. The geometry of the micelles determined from this transport studies is in good agreement with cyclic voltammetry and DLS studies [36,37].

REFERENCES

1. I. R. Schmolka, J. Am. Oil Chem. Soc., 54, 110 (1977).
2. P. Bahadur and G. Riess, Tenside Surf. Det., 28, 173 (1991).
3. B. Chu, Langmuir, 11, 414, (1995).
4. P. Alexandridis and T. A. Hatton, Colloids Surf. A: Physicochem. Eng. Aspects, 96, 1 (1995).
5. G. wanka, H. Hoffmann and W. Ulbricht, Macromolecules, 27, 4145 (1994).
6. M. Malmsten and B. Lindman, Macromolecules, 25, 5440 (1992).
7. J. T. Li and K. D. Cadwell, Colloids Surf. B., 7, 9 (1996).
8. S. Stolnik, N. C. Felumb, C. R. Heald, M. C. Garnett, L. Illum and S. S. Davis, Colloids Surf. A., 122, 151 (1997).
9. M. Svensson, P. Linse and F. Tjerneld, Macromolecules, 28, 3597 (1995).
10. Y. Zheng and H. T. Davis, Langmuir, 16, 6453 (2000).
11. S. Forster and E. Kramer, Macromolecules, 32, 2783 (1999).
12. H. P. Henze, E. Kramer, B. Berton, S. Forster, M. Antonietti and M. Dreja, Macromolecules, 32, 5803 (1999).
13. Z. Zhou and B. Chu, J. Colloid Interface Sci., 126, 171 (1988).
14. N. K. Reddy, P. J. Fordham, D. Attwood and C. Booth, J. Chem. Soc. Faraday Trans., 86, 1569 (1991).
15. K. Mortensen, Europhys.Lett., 19, 599 (1992).
16. M. Almgren, W. Brown and S. Hvidt, Colloid Polym. Sci., 273, 2 (1995).
17. G. Karlstrom, J. Chem. Phys., 89, 4962 (1985).
18. M. Andersson and G. Karlstrom, J. Chem. Phys., 89, 4957 (1985).
19. P. Linse, Macromolecules, 26, 4437 (1993).
20. P. Linse, J. Phys. Chem., 97, 13896 (1993).
21. P. N. Hurter, J. M. H. M. Scheutjens and T. A. Hatton, Macromolecules, 26, 5030 (1993).

22. P. Alexandridis, J. F. Holzwarth and T. A. Hatton, Macromolecules, 27, 2414 (1994).
23. T. Nivaggioli, B. Tsao, P. Alexandridis and T. A. Hatton, Langmuir, 11, 119 (1995).
24. P. Alexandridis, T. Nivaggioli and T. A. Hatton, Langmuir, 11, 1468 (1995).
25. P. R. Desai, N. J. Jain, R. K. Sharma and P. Bahadur, Colloids and Surf. A., 178, 57 (2001).
26. B. Geetha, A. B. Mandal and T. Ramasami, Macromolecules, 26, 4083 (1993).
27. B. Geetha and A. B. Mandal, J. Chem. Phys., 105, 9649 (1996).
28. B. Geetha and A. B. Mandal, Chem. Phys. Lett., 266, 443 (1997).
29. B. Geetha and A. B. Mandal, J. Surface Sci. Technol., 17, 29 (2001).
30. B. Geetha and A. B. Mandal, Langmuir, 11, 1464 (1995).
31. B. Geetha and A. B. Mandal, Langmuir, 13, 2410 (1997).
32. B. Geetha and A. B. Mandal, Chem. Phys., Lett., 318, 35 (2000).
33. B. Geetha and A. B. Mandal, Langmuir, 16, 3957 (2000).
34. A. B. Mandal, S. Ray, A. M. Biswas and S. P. Moulik, J. Phys. Chem., 84, 856 (1980).
35. A. B. Mandal, S. Gupta and S. P. Moulik, Ind. J. Chem., 24A, 670 (1985).
36. J. James, S. Vellaichami, R. S. G. Krishnan, S. Samikannu and A. B. Mandal, Chem. Phys., 312, 275 (2005).
37. J. James, C. Ramalechume and A. B. Mandal, Chem. Phys. Lett., 405, 84 (2005).
38. A. B. Mandal and B.U. Nair, J. Phys. Chem. 95, 9008 (1991).
39. A. B. Mandal and S. P. Moulik, “ACS Proceedings in: Solution Behavior of Surfactants-Theoretical and Applied Aspects”, Eds., K. L. Mittal,; E. J. Fendler,: Plenum Press, New York, 1982, Vol.1, pp. 521-541.
40. A. B. Mandal, B. U. Nair and D. Ramaswamy, Langmuir, 4, 736 (1988).
41. A. B. Mandal, Langmuir, 9, 1932 (1993).
42. A. B. Mandal, D. V. Ramesh and S. C. Dhar, Eur. J. Biochem., 167, 617 (1987).
43. C. Rose and A. B. Mandal, Int. J. Biolog. Macromolecules, 18, 41 (1996).
44. R. S. G. Krishnan, S. Thennarasu and A. B. Mandal, Chem. Phys., 291, 195 (2003).
45. M. Kanthimathi, K. Deepa, B. U. Nair and A. B. Mandal, Bull. Chem. Soc. Jpn., 73, 1769 (2000).
46. B. L. Bales and M. Almgren, J. Phys. Chem., 99, 15153 (1995).
47. R. S. G. Krishnan, S. Thennarasu and A. B. Mandal, J. Phys. Chem. B., 108, 8806 (2004).

48. (a) S. P. Moulik. Electrochim Acta, 18, 981 (1973); (b) S. P. Moulik and D. P. Khan, Carbohyd. Res., 36, 147 (1974).
49. H. Eyring, in Rheology of Polymers, edited by G. V. Vinogradov and A. Ya. Malkin, Mir Publications, Moscow, Ch.2, p.106, 1980.
50. R. J. Robson and E. A. Dennis, J. Phys. Chem., 81, 1075 (1977).