Chapter V

Investigation of the Properties of Decaoxyethylene n-Dodecyl Ether, $C_{12}E_{10}$ in Aqueous Sugars-rich Region

ABSTRACT

Interfacial, thermodynamic and morphological properties of decaoxyethylene monododecyl ether $[CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH]$, $C_{12}E_{10}$ in aqueous solution were analyzed by tensiometric, viscometric, proton NMR and small-angle neutron scattering (SANS) techniques. Dynamic and structural aspect at different temperatures in the absence and presence of sugars at different concentrations were measured. Critical micelle concentration (CMC) was determined by the surface tension measurement in presence of ribose, glucose and sucrose. The heat capacity ($\Delta C_{p.m}$), transfer enthalpy ($\Delta H_{m.tr}$), transfer heat capacities ($\Delta C_{p.m.tr}$), micellization constant (K_m), Setchenow constant (K_S^N) and partition coefficient (q) were determined and discussed as an extension of the usual thermodynamic quantities of micellization and adsorption at the air-water interface. An enthalpy-entropy compensation effect was observed with an isostructural temperature (Tc) of about 310K for both micellization and the interfacial adsorption. SANS measurements were taken to elucidate the structural information *viz.* aggregation number (N_{agg}), shape, size and number density (N_m) of $C_{12}E_{10}$ micelle in D_2O at different concentrations of sugars (0.05, 0.02, 0.3, and 0.5M) and temperatures (30, 45 and 60°C). Intrinsic viscosity gives the hydrated micellar volume (V_h), volume of the hydrocarbon core (V_c) and the volume of the palisade layer of OE unit (V_{OE}). SANS as well as rheological data support the formation of non-spherical micelle with or without sugars. By SANS, we also observed that at the studied temperature intervals, oblate ellipsoid micelle changed into prolate ellipsoid and the number density of micelles decreased with an increase in the temperature both in the presence and in the absence of sugars and also on increasing the concentration of sugars. Proton NMR showed a change in chemical shift of OE group of micelle above the CMC. We also studied phase separation of $C_{12}E_{10}$ by sugars in cloud point measurements.

Surfactant molecules self assemble into finite-sized aggregates called micelle in aqueous solution. These are significant for their numerous uses including solubilization, dispersion, emulsification, catalysis, and technological, biological and pharmaceutical applications. Such aggregates are formed in various shapes, e.g. globular, ellipsoidal, cylindrical and disc like (1). The morphology of micelles depends on the chemical structure of surfactant monomer (2) and the solution conditions like concentration, temperature, co-surfactant and ionic strength (3,4). Control of the morphology of such aggregates by the addition of external additives or by proper choice of surfactant mixture has become increasingly important in recent years, both from a theoretical and from an experimental points of view.

To achieve a deep understanding of physicochemical properties of micelle, their dynamic and morphological properties must be achieved simultaneously (5). No single technique is capable of yielding both types of information unambiguously; thus, there is a need to combine both types of studies in order to gather the information. The aggregational and surface properties of surfactant in solution are very sensitive and are influenced or tuned to desired range and application by altering the solvent polarity and type, temperature, pressure, *p*H and presence of various foreign substances (co-solvent) (6-14). The nature of co-solvent determines the direction in which the changes in the critical micelle concentration (CMC) of the surfactants occur. The co-solvents may be distributed between an aqueous and micellar phase and may accumulate both in palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. Electrolytes generally decrease the CMC (14b), nonelectrolytes may increase or decrease (15-17), some organic co-solvents, when present in greater amounts, even cause disappearance of the micelles (14c).

The effect of sugars *viz.*, glucose (18-21), fructose (18,21) and sucrose (10,12,21,22) on the micellization process has been studied. However, some aspects warrant further investigation. Blandamer *et al.* (19) found that, by adding glucose, fructose and arabinose to the micellar catalyzed reaction of 2,4-dinitrochlorobenzene with hydroxide ions, the first order rate constant increased, indicating an enhancement of the catalytic action of cetyltrimethylamonium bromide (CTAB). However they mentioned that attempts to measure the effect of sugars on the CMC of CTAB proved unsuccessful.

Most of the publications referenced above, address the possible effect of sugars on ionic surfactants, whereas few describe the effect on nonionic (10,12,22,23). However, no comprehensive thermodynamic and morphological study of n-dodecyloligo ethylene oxide nonionic surfactant, $C_{12}E_{10}$ in presence of sugars has been identified. Sugars are chosen because they are the stuff of life for most organisms (24), they are nonionic. Consequently, whatever effects are observed would be mainly chemical in nature and not electrochemical. Alkyl polyoxyethylene-type nonionic surfactants were chosen because they are widely used in detergency; cosmetics; fabric softening; emulsion formulations like shampoos, conditioners, paints, pharmaceutical dosages; and drug delivery systems, and their use will continue in the future owing to their higher solubility at low temperatures. Moreover, the additive effect was expected to cause low CMC values, which will reduce the total amount of surfactant, thereby lowering the cost and toxicity.

Interfacial, thermodynamics, small-angle-neutron scattering (SANS), viscosity, cloud point and ^1H nuclear magnetic resonance (NMR) properties of $C_{12}E_{10}$-aqueous-sugars ternary system were studied to help in understand the interaction of non-ionic additives with nonionic surfactants.

EXPERIMENTAL PROCEDURES

Materials

$C_{12}E_{10}$ was commercially available product (Sigma, St. Louis, MO) and was used without further purification. Owing to polydispersity in the number of oxyethylene (OE) units, it was not a pure sample, as was mentioned by Dorsey *et al.* (25). However the surface tension-concentration plots at a given temperature did not show any minimum. D-Ribose ($C_5H_{10}O_5$), D-Glucose ($C_6H_{12}O_6$) and Sucrose ($C_{12}H_{22}O_{11}$) (Merck, Darmstadt, Germany) were dried in *vacuo* before use. For analysis of physicochemical properties, all solutions were prepared by using triple distilled deionized water showing electric conductance 2-3 μS cm^{-1} at 303K. For the SANS study, 99.4% D_2O (Heavy Water Division, BARC, Mumbai) was used, and for ^{1}H NMR, 99.8% D_2O (Merck) was used. D_2O was used instead of water when preparing solutions for the SANS experiments to provide a very good contrast between the micelles and the solvent.

Surface tension measurements

Surface tension (γ) was measured by a du-Noüy ring tensiometer (S. C. Dey and Co., Kolkata, India) at different temperatures (308, 313, 318 and 323K) and in sugar solutions of various concentrations (wt/vol) *viz.* 0.25, 0.5, 0.75, and 1.0%. Temperatures were constant (±0.1K) by circulating thermostated water through a jacketed vessel containing the solution. Other conditions were same as reported in our recent papers (26,27). Representative plots of γ vs. $\log_{10}$ C isotherms are shown in Figure 1.

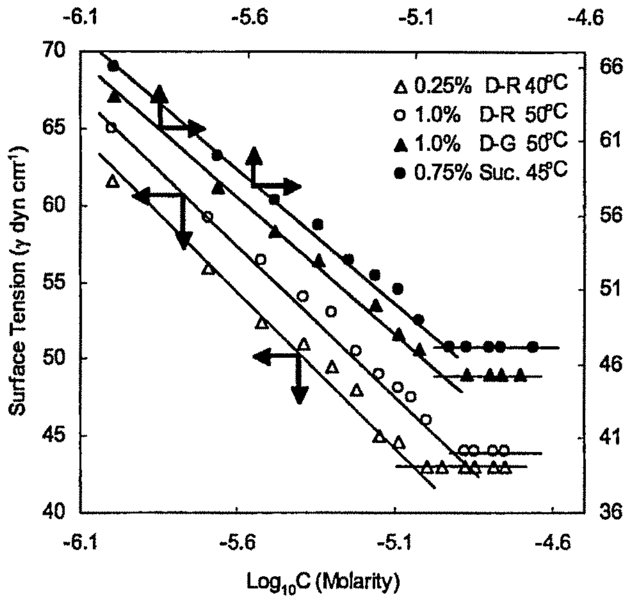

FIG 1. Representative plots of surface tension (γ) vs. $Log_{10}C$ (Molarity) in the presence of sugars.

SANS measurements

SANS is well-known ideal technique for studying micellar morphology (28,29) and this also has been also demonstrated for surfactant micelle in the presence of various additives (30-35). SANS experiments were performed on the SANS spectrometer at the Dhruva reactor, Trombay, Mumbai, India (36). The spectrometer used a BeO filter as a monochromator beam and had a resolution ($\Delta Q/Q$) of about 15% at $Q=0.05Å^{-1}$. The scattered neutrons were detected in an angular range of $0.5\text{-}15^{0}$with a linear position-sensitive detector (PSD). The accessible wave vector transfer, Q ($=4\pi Sin\ \theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident neutrons), in the spectrometer was $0.02\ Å^{-1}$ to $0.32\ Å^{-1}$. The wavelength of neutrons used for these experiments was usually between 4 and 10 Å. The PSD allowed simultaneous recording of the data over the full Q range. Each solution was held in a 1.0-cm-path length ultraviolet-grade quartz cell with tight-fitting Teflon stopper that was sealed with Parafilm. The spectra were recorded at 30, 45 and 60°C (±0.2°) while keeping the quartz cell between metal heaters. The sample-to-detector distance was 1.8m for all runs. The intensities were normalized to an absolute cross-section unit. Thus, plots of a cross-section per unit volume ($\partial\Sigma/\partial\Omega$) vs. scattering vector (Q) were obtained. The experimental points were fitted using a nonlinear least square method. Both the semi-major axis (a) and semiminor axis ($b = c$) were fitting parameters. The volumes of the monomeric surfactants, calculated from the density and molecular weight of the corresponding hydrocarbon and then by dividing the molar volume of the hydrocarbon by Avogadro's number (N_A), were 381.4, 388.2 and 395.3 Å^3/molecule at 30, 45 and 60°C respectively. The aggregation number (N_{agg}) for the micelle was related to the micellar volume (V_{m}) by the equation, $N_{agg}=V_m/ v$ (37), where $V_m = 4/3\pi a b^2$ and v is the volume of the single surfactant monomer at a given temperature. From the calculated values of N_{agg}, the number density of micelles, N_{m} is calculated by the following equation:

$$N_{\mathrm{m}}\,/\mathrm{cm}^{-3} = \frac{(\mathrm{C{-}CMC})\,\mathrm{x}10^{3}N_{\mathrm{A}}}{N_{\mathrm{agg}}} \qquad [1]$$

where C are the concentration of surfactant in mole l^{-1}. It was assumed that the micelle has an inner core consisting of hydrophobic part and an outer shell that contained ether and the water of hydration. Intermiceller interference effects were neglected, and the measured distributions were analyzed in terms of the form factor of an ellipsoid.

Data treatment

SANS data were corrected for background, empty cell scattering and, sample transmission factors. The corrected intensities were normalized to absolute cross-section units; thus, the coherent differential scattering cross-section per unit volume, $\partial\Sigma/\partial\Omega$, vs. Q was obtained. The absolute calibration has an estimated uncertainty of 5%. Experimental data points were fitted using a nonlinear least square routine as described next. Comparisons between the experimentally obtained and theoretically calculated cross-sections are shown in Figures 4 - 7.

SANS data Analysis

For a system composed of monodispersed, uniform ellipsoidal colloidal particles, the coherent differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) is given by

$$d\Sigma/d\Omega = n\,(\rho_p - \rho_s)^2\, V^2 P(Q)\, S(Q) \qquad [2]$$

where n denotes the number density of particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intraparticle-structure factor and is established by the shape and size of the particle. $S(Q)$ is the interparticle-structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions. For dilute solutions, interparticle interference effects were negligible. Measurements were taken at low concentration such that $S(Q) \sim 1$ and $P(Q)$ were calculated for ellipsoidal micelles. The dimensions of the micelles, aggregation number and number density of micelles were determined from the analysis. The semimajor axis (a) and semiminor axis (b=c) were the parameters used in analyzing the SANS data. We found that the experimental SANS intensity best matched the values obtained using an ellipsoidal model. In all the measurements, the concentration of $C_{12}E_{10}$ (50mM) is held constant and the concentration of sugars (0.05,0.1,0.2,0.3M) and the temperature (30, 45 and 60°C) were varied. Further experimental details and theoretical expressions for data treatment were identical to those described previously (38).

Viscosity measurement

The viscosity of surfactant solution was effected by the interaction of both the hydrophobic core and hydrophilic outer shell of the micelle with water. It measured the solute-solvent interaction and the shape and size of the micelle.. The latter were effected by temperature changes. Thus, the viscosity of the $C_{12}E_{10}$ (50mM) surfactant solution was determined in the absence and presence of sugars and at the same temperatures as for the SANS measurements. The flow time of surfactant solution and water was measured using an Ubbelohde suspended-level viscometer. The density of surfactant solution was determined with a pyncnometer. Density and viscosity measurements were carried out in a thermostated water bath (±0.1°C). Samples were carefully filtered before injection into viscometer. Three consecutive flow times agreeing within ± 0.02s were taken and the mean flow time was considered. The intrinsic viscosity, $|\eta|$, was calculated using the relation,

$$|\eta| = \lim_{C \to 0} (\eta_r - 1)/C \qquad [3]$$

where limit to zero concentration indicates that intermolecular interactions were absent and η_r indicates the relative viscosity of the surfactant solution. Some researchers (39,40) have taken $|\eta|$ to be equal to $(\eta_r - 1)/C$ without the condition of limiting concentration. In this article, $|\eta|$ was calculated without taking the zero concentration limit into the account as in previous work (27).

Cloud point (CP)

Phase separation of the surfactant solution was studied by determination the CP of $C_{12}E_{10}$ (1% wt/vol) in the presence of an increasing amount of sugar, as described previously (11). The CP was an average of the temperature at which clouding appeared and then disappeared. These temperatures did not differ by greater than ±0.2°C.

NMR Measurement

^{1}H NMR measurements of $C_{12}E_{10}$: sugars, (1:1 wt/vol) were carried out at room temperature (25°C ±0.5) by Bruker Advance 300 spectrophotometer (Nruker, Karlsruhe, Germany) operating at 300 MHz.

RESULTS AND DISCUSSION

Thermodynamic of micellization and interfacial adsorption of $C_{12}E_{10}$ Interaction with sugars:

Surface tension is a fast, nondestructive and dependable means of determining the CMC (41). The CMC values of $C_{12}E_{10}$ in presence of sugars at different temperatures are presented in Table 1.

TABLE 1. Critical Micelle Concentration (CMC) of $C_{12}E_{10}$ in Presence of Sugar at Different Temperatures.

Conc.of sugar	Critical micelle concentration (μ M)			
(%)	308	313	318	323 K
D-ribose				
0.0	11.8 ±0.12	10.0 ±0.10	8.9 ±0.09	7.1 ±0.07
0.25	7.4 ±0.08	8.3 ±0.08	8.9 ±0.09	9.3 ± 0.09
0.5	7.5 ±0.08	8.1 ±0.08	9.1 ±0.09	10.2 ±0.10
0.75	7.9 ±0.08	8.7 ±0.09	9.3 ±0.09	10.0 ±0.10
1.0	7.9 ±0.08	8.9 ±0.09	9.6 ±0.10	10.9 ±0.11
D-glucose				
0.25	7.1 ±0.07	8.1 ±0.08	8.9 ±0.09	9.1 ±0.09
0.5	7.3 ±0.07	8.3 ±0.08	8.5 ±0.09	9.0 ± 0.09
0.75	7.6 ±0.08	8.7 ±0.09	9.5 ±0.10	10.0 ±0.10
1.0	8.1 ±0.08	8.9 ±0.09	9.8 ±0.10	10.0 ±0.10
Sucrose				
0.25	6.7 ±0.07	7.1 ±0.07	8.1 ±0.08	8.9 ±0.09
0.5	7.1 ±0.07	7.9 ±0.08	8.1 ±0.08	8.9 ±0.09
0.75	7.2 ±0.07	8.1 ±0.08	8.9 ±0.10	9.5 ±0.10
1.0	7.9 ±0.08	8.1 ±0.08	8.9 ±0.10	9.3 ±0.09

The CMC value without any additive, at a particular temperature was in good agreement with the values in the literature (9,10,14a, 40). The CMC values of $C_{12}E_{10}$ were found to decrease with an increase in temperature in absence of sugars, consistent with observations in a previous work (8). The presence of sugars had almost the same effect, i.e., there was a decrease in the CMC at a lower temperature. From the experimental results, it seems two antagonistic effect of structure making and structures breaking were happening simultaneously in the system in presence of sugars. Sugars are water-structure maker and, owing to their larger number of hydroxyl groups, sucrose is a better structure maker than ribose and glucose. In the case of OE micelles, the head group will be strongly hydrated. In the presence of sugars, the sugars may interact with the surfactants or simply replace some of the water molecules of the hydrated OE groups, affecting the repulsive interaction between the head groups. Under such condition, the CMC of $C_{12}E_{10}$ increases when sugars concentration is increased. In presence of sugars the CMC increase with increasing temperature in all cases studied. This was observed earlier in presence of different additives (9,10,42). For a nonionic surfactant without any additive, the CMC decreased with an increase in temperature owing to the dehydration of the hydrophilic moiety of the surfactant molecule caused by a breaking of water structure. In the presence of additive, however, the reverse was seen, indicating that these molecules significantly alter the micellization process. As shown in Table 1, increasing the number of OH groups in the sugars decreased the CMC values, particularly at higher temperature. Sugars form intermolecular hydrogen bonds with the solvent water molecules and thereby promote the water structure, which is also promoted by the hydrophobic parts of the surfactant molecule through hydrophobic interaction. In the presence of additives, the water structure is broken as the temperature increases, but aqueous-sugar structure are formed. Consequently, there is overall structure formation and the CMC increases.

The Gibbs free energy of micellization (ΔG^{o}_{m}) for a nonionic surfactant is directly proportional to the ln X_{CMC} (CMC in mole fraction scale) at constant temperature by the relation (4) $\Delta G^{o}_{m}=RT \ln X_{CMC}$. The initial standard state being a hypothetical, where the surfactant molecules are in mole fraction units and behaving as though they are at infinite dilution, and the final state being the micelle itself. In Table 2 the ΔG^o_m, ΔH^o_m, and ΔS^o_m at the standard state of mole fraction unit at 45°C are reported in presence of various amount of sugars. In the absence of additives, the free energy of micellization becomes more negative with an increasing temperature. That is, the formation of micelles become relatively more spontaneous at higher temperature. Even in the presence of sugars the variation is similar though the CMC increase with temperature. The reason for such an observation has been given earlier (10).

TABLE 2 Thermodynamic and Transfer Heat parameters of Micellization of $C_{12}E_{10}$ Aqueous Solution in Presence of Sugar at 45°C.

Conc. of Sugar % D-ribose	$-\Delta G^\circ_m$ ($kJmol^{-1}$)	ΔH°_m ($kJmol^{-1}$)	ΔS°_m ($Jmol^{-1}K^{-1}$)	$\Delta C_{p\,m}$ ($Jmol^{-1}K^{-1}$)	$-\Delta H_{m.tr}$ ($kJmol^{-1}$)	$\Delta C_{p\,m.tr}$ ($Jmol^{-1}K^{-1}$)
0.0	40.4	20.95	196	-0.120	-	-
0.25	41.4	-12.6	90.4	-0.003	33.6	0.117
0.50	41.3	-16.8	77.0	-0.001	37.8	0.119
0.75	41.3	-12.8	89.6	-0.003	33.8	0.117
1.0	41.2	-17.2	75.2	-0.006	38.2	0.114
D-glucose						
0.25	41.4	-14.0	86.4	-0.005	35.0	0.115
0.50	41.5	-10.9	96.0	-0.001	31.9	0.119
00.75	41.2	-15.0	82.6	-0.002	36.0	0.118
1.0	41.1	-11.9	92.2	-0.005	32.9	0.115
Sucrose						
0.25	41.6	-16.5	78.8	-0.002	37.5	0.118
0.50	41.6	-15.6	81.6	-0.012	36.6	0.108
0.75	41.4	-10.6	97.2	-0.001	31.6	0.119
1.0	41.4	-9.5	100.2	-0.002	30.5	0.118

(The error in the data is <2%)

The standard enthalpy of micellization (ΔH^o_m) and the standard entropy of micellization (ΔS^o_m) were computed from the reasonably linear ΔG^o_m vs. T plots, the slope being ΔS^o_m. The ΔH^o_m was then computed by using the following equation (4):

$$\Delta H^o_m = \Delta G^o_m + T\Delta S^o_m \qquad [4]$$

The process of micellization was endothermic, although it became exothermic in the presence of sugars. The exothermicity may be due to additive-surfactant attractive interaction (4), which result in the stability of the system. The exothermic and endothermic characteristics of micellization are specific to the surfactant, the additive and the temperature of micellization, although they were independent of temperature in the present system. The entropy of micellization (ΔS^o_m) was positive, indicating that the micellization process was somewhat entropy-dominated in the absence of sugars. However, it should be noted that the micellization process was exothermic in these systems; therefore the formation of micelle was very much favored in presence of sugars. Rosen (8) has stated that the presence of hydrated OE groups of the surfactant introduces structure in the liquid phase and that the removal of the surfactant *via* micellization result in an increase in the overall randomness and hence an increase in entropy. Micelle formation also frees water molecules due to the absence of hydrophobic interaction and release of the so called 'iceberg' water.

A linear correlation between ΔH^o_m and ΔS^o_m was observed in all these systems (Fig. 2). Such a relationship was suggested by Lumry and Rajender (43). The slope of the line, i.e., the compensation temperature (T_c) was found to be 318 K in aqueous medium, higher than the expected 270 to 294 K (43). The small variations, we observe here and in an earlier work (15) may be due to the difference of the bulk structural property of the solution compared with water. However, deviations from such a linear relationship are well known. As mentioned by Krug *et al.* (44), error in the data may also lead to such compensation. This type of relationship is discussed in an in an earlier publication (45).

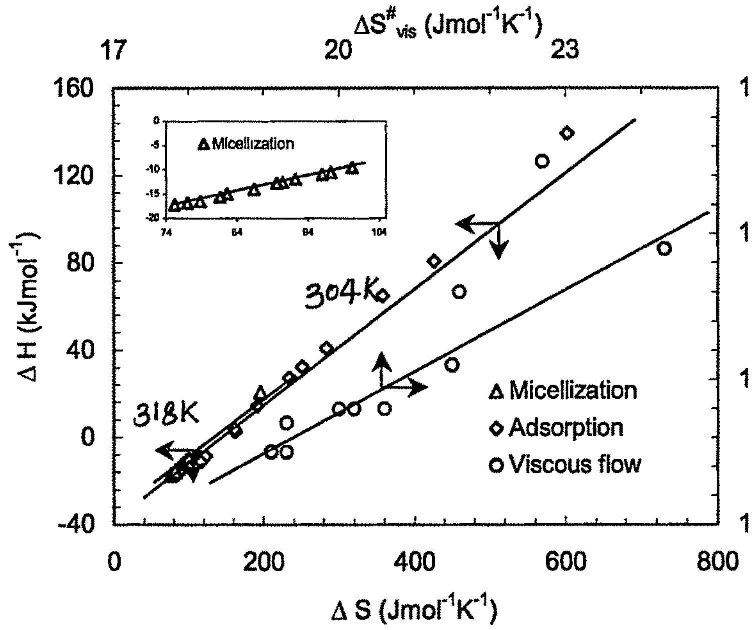

Figure 2. Enthalpy-entropy compensation plot for all systems together.

The heat capacities for the micelle formation ($\Delta C_{p.m.}$) were also evaluated from the plot of ΔH_m vs. T, the slope being $\Delta C_{p.m.}$ (Table 2). The variation of heat capacities with concentration of the additives did not show regularity in any of the assessments. The transfer enthalpies ($\Delta H_{m.tr}$) and transfer heat capacities $\Delta C_{p.m.tr.}$) of micelle from water to aqueous solution were obtained using the relation

$$\Delta H_{m.tr} = \Delta H_{m.}(\text{aq.additive}) - \Delta H_m(\text{aq.}) \qquad [5]$$

$$\Delta C_{p.m.tr.} = \Delta C_{p.m}(\text{aq.additive}) - \Delta C_{p.m.}(\text{aq.}) \qquad [6]$$

The transfer enthalpies of micelle were found to be negative (Table 2). Negative transfer enthalpies also were reported for the transfer of NaCl and amino acids from water to aqueous urea solution (14,46). This shows that transfer of hydrophilic (OE) groups from water to aqueous-sugars solution was exothermic, whereas that of hydrophobic group was endothermic. The strong OE-sugars interaction was the dominating cause. The transfer heat capacities of micellization $\Delta C_{p.m.tr.}$ for the transfer of micelle from water to additive containing solution were positive, Suggesting increased hydration of the micelles attributable to increased hydrogen bonding between OE and sugars present in the solution. The $\Delta C_{p.m.tr.}$ values remained more or less constant over all systems, suggesting no obvious structural transition.

Sulthana *et al.* (9) showed that for dilute solutions of polar additives in an aqueous surfactant solution at CMC, the following general form of classical Setchenow equation was well obeyed

$$\log CMC_w / CMC_{w+A} = K_M m' \qquad [7]$$

where CMC_w and CMC_{w+A} are the CMC values of surfactant in the absence and in the presence of additives, K_M is a micellization constant and m' is the molarity of the additive. In a dilute solution with respect to polar additive, the constant K_M takes the form

$$K_M = ½ [k_s^N + qM / 2.303 \times 1000] \qquad [8]$$

where k_s^N is the Setchenow constant or salting out constant, q is the ideal partition coefficient of the solute between the micelle and water, and M is the molecular weight of the solvent. The salting constant is calculated by the empirical relationship

$$k_s^N = 0.637–0.014n\ (CH_2) – 0.146R \qquad [9]$$

where n (CH_2) is the number of methylene groups in the linear hydrocarbon chain and R is the hard-sphere diameter of the additives calculated from Van der Waals volumes. The R values for D-ribose, D-glucose and sucrose are 6.06, 6.56 and 8.04 $Å^3$ respectively (47).

The k_s^N values calculated for all three additives were negative, indicating a salting-in effect in aqueous surfactant solution. The K_M values obtained at all ratio of sugars are given in Table 3 .

TABLE 3 Micellization Constant *K*m (Lmol^{-1}) for $C_{12}E_{10}$ in Presence of Sugar at Different Temperatures.

Sugar	308	313	318	323K
D-ribose	-0.64	-0.73	-0.65	-1.18
D-glucose	-1.36	1.03	-1.25	-1.21
sucrose	-3.04	-2.53	-2.26	-1.19

(The error in the data is <2%)

The ideal partition coefficient, *q*, obtained using the K_M and k_s^N values tended toward Zero for all the systems. Such a *q* value suggests that the additives did not penetrate the micelle, i.e., the additives were not partitioned between the micelle and the solvent. Therefore, the variation in the CMC with the addition of these solutes can be entirely ascribed to the effect of these additives on the bulk solvent properties. The solvent molecules induce a shift in the equilibrium between the micelles and surfactant monomers in favor of the latter by their interaction with both the surfactant monomers and the solvent molecules. Since these additives did not penetrate, they can probably be assumed to locate themselves at the micelle-solvent interface. In other words, a large amount of the additives was present in the solvent, which was in contact with the hydrophilic group of the micelle. These results were supported by NMR and SANS data, as discussed later.

The air-water interface of a surfactant solution is well populated by the adsorbed molecules. The maximum surface excess (Γ_{max}) is an effective measure of adsorption at the air-water interface and was calculated by Gibbs adsorption equation (8). Γ_{max} was calculated from the limiting area per molecule (A_{min}) values (26). The slope of the tangent at the given concentration of the γ vs. log*C* plot (i.e., $d\gamma/d\log C$) was used to calculate Γ_{max}, by fitting a curve to a polynomial of the form, $y = ax^2 + bx + c$ in Microsoft excel. The regression coefficient (R^2) value for the fit was between 0.9673 and 0.9996. The Γ_{max} increased with an increase in temperature (Table 4). This resulted from a decrease in the hydration of the ethoxy segment of the nonionic surfactant as the temperature increased; hence, the tendency to locate at the air-water interface was higher. The magnitude of A_{min} was much lower than 1.5 nm^2 (data not given), suggesting that the air-water interface was closely packed and the orientation of the surfactant molecule was almost perpendicular to the surface.

The effectiveness of a surface-active molecule was measured by surface pressure (π_{CMC}) at the CMC, i.e., $\pi_{CMC} = \gamma_o - \gamma_{CMC}$, where γ_o and γ_{CMC} are the surface tension of pure water and surface tension of surfactant solution at CMC respectively. The value of free energy of adsorption at air/water interface (ΔG^o_{ad}) was calculated using the relation (8,9)

$$\Delta G^o_{ad} = RT \ln CMC - N \pi_{CMC} A_{min} \qquad [10]$$

TABLE 4 Maximum Surface Excess (Γ_{max}) and Traube′ s constant (x 10^{-7}) of $C_{12}E_{10}$ in the Presence of sugar at Different Temperatures.

Conc. of Sugar (%)	Γ_{max}x 10^{10}(mol cm^{-2})											
	D-ribose				D-glucose				sucrose			
	308	313	318	323	308	313	318	323	308	313	318	323K
0.0	2.3	2.4	3.3	3.6	-	-	-	-	-	-	-	-
	(5.5)	(68.6)	(125)	(19.0)								
0.25	3.9	4.1	3.7	3.6	2.2	2.2	2.6	4.3	4.2	5.5	2.5	2.8
	(7.3)	(10.1)	(6.7)	(10.5)	(7.3)	(1.8)	(3.9)	(3.4)	(4.2)	(5.9)	(7.5)	(5.6)
0.50	2.6	2.5	1.8	1.6	2.9	2.3	2.6	2.3	2.8	3.0	2.6	2.8
	(21)	(8.9)	(57.8)	(25.7)	(11.7)	(3.3)	(9.1)	(5.2)	(8.2)	(8.3)	(12.9)	(12.2)
0.75	2.7	2.7	4.4	2.4	2.5	2.5	3.6	3.2	3.6	4.2	2.9	2.3
	(14.8)	(9.0)	(5.3)	(16.4)	(15.4)	(4.6)	(10.0)	(6.9)	(4.3)	(4.3)	(12.9)	(10.1)
1.0	2.8	2.8	4.3	4.1	2.4	3.1	2.1	2.4	2.8	2.3	3.3	3.6
	(7.6)	(5.2)	(3.9)	(4.6)	(24.9)	(10.1)	(13.4)	(17.0)	(7.7)	(7.7)	(8.1)	(6.7)

Value in parenthese are Traube′ s constant (x 10^{-7})

(The error in the data is <2%)

TABLE 5 Thermodynamic of Adsorption and Sugar Structural Effect on Micellization and Adsorption parameters of $C_{12}E_{10}$ Aqueous Solution at 45°C.

Conc. of sugar %	$-\Delta G^{\circ}_{ad}$ ($kJmol^{-1}$)	ΔH°_{ad} ($kJmol^{-1}$)	ΔS°_{ad} ($Jmol^{-1}K^{-1}$)	ΔG°_{m}- ΔG°_{ad} ($kJmol^{-1}$)	ΔH°_{m}- ΔH°_{ad} ($kJmol^{-1}$)	$T(\Delta S^{\circ}_{m}-\Delta S^{\circ}_{ad})$ ($kJmol^{-1}$)
D-ribose						
0.0	54.5	81.0	426	14.1	-60.0	-73.1
0.25	46.9	27.5	234	5.5	-40.1	-45.7
0.50	52.5	139.3	603	11.2	-156.1	-167.3
0.75	46.3	14.8	192	5.0	-27.6	-32.6
1.0	45.5	-13.7	100	4.3	-3.5	-7.9
D-glucose						
0.25	45.5	-8.9	115	4.1	-5.1	-9.1
0.50	47.7	-8.6	123	6.2	-2.3	-8.6
00.75	48.0	-11.1	116	6.8	-3.9	-10.6
1.0	48.7	2.8	162	7.6	-14.7	-22.3
sucrose						
0.25	47.2	32.6	251	5.6	-49.1	-54.7
0.50	48.6	41.1	283	7.0	-56.7	-64.0
0.75	48.6	65.2	358	7.2	-75.8	-83.0
1.0	47.4	3.8	161	6.0	-13.3	-19.2

(The error in the data is <2%)

Table 5 presents the thermodynamic parameters of adsorption, i.e., ΔG^{o}_{ad}, ΔH^{o}_{ad} and ΔS^{o}_{ad} of $C_{12}E_{10}$ in the presence of sugars at air-water interface at 45°C. The ΔG^{o}_{ad} values are negative throughout, indicating that the adsorption of the surfactant at the air-water interface takes place spontaneously in the presence or absence of sugars. The standard entropy (ΔS^{o}_{ad}) and enthalpy (ΔH^{o}_{ad}) of adsorption were obtained from the slope of the ΔG^{o}_{ad} –T plot. As expected, ΔG^{o}_{ad} values were more negative than their corresponding ΔG^{o}_{m}, indicating that when a micelle was formed, work has to be done to transfer the excess surfactant molecules present in the monomeric form at the surface to the micellar stage through the aqueous medium. Under this condition the interface was saturated with monomeric surfactant molecules.

ΔG^{o}_{ad} becomes more negative, with an increase in temperature (data not shown) in either the presence or absence of additives, suggesting that the adsorption at higher temperature was more facile. ΔH^{o}_{ad} in pure aqueous solution was positive, as was ΔH^{o}_{m}. However. in the presence of sugars, the results did not in follow a regular trend. This suggests that these additives interact with the hydrophilic group of surfactant, which was exothermic, as was shown earlier for NaCl by Jha and Ahluwalia (46). The ΔS^{o}_{ad} in pure aqueous solution and in the presence of sugar additives was positive. This may be ascribed to a larger freedom of motion of the hydrocarbon chain at the interface and also the mixing of surfactant monomers with additive molecules. A linear correlation between ΔH^{o}_{ad} and ΔS^{o}_{ad} was observed in all the system having a T_c 304K (Figure 2). However, one must remain conscious of the limitations of the observation, as has been discussed.

Weiner and Zografi (48) suggest that

$$\Delta G^{o}_{ad} = -RT \ln \sigma \qquad [11]$$

where 'σ 'is known as Traube's constant (6) and is defined by the relation

$$\sigma = (\partial \pi / \partial C)_{C \to 0} = -(\partial \gamma / \partial C)_{C \to 0} \qquad [12]$$

This means σ is the rate of change of surface pressure per unit concentration change at infinite dilution. The σ values are given in Table 4. One can note that the σ of the pure $C_{12}E_{10}$ given in Table 4 is similar to the data of Uneno *et al.* (49), thereby suggesting the adsorption data were reasonable. When the effect of different sugars on σ was computed, little difference in σ values was observed as a function of sugars, probably because the sugars concentrations are not very high.

SANS Studies of $C_{12}E_{10}$: Effect of sugars and temperature on the $C_{12}E_{10}$ micellar structure.

The experimental and theoretically fitted results of SANS for $C_{12}E_{10}$ micellar solution are shown in Figures 3-6, and the estimated structural parameters, i.e., aggregation number (N_{agg}), semi-major (a), semi-minor (b=c), axial ratio (a / b) and number density of micelle (N_m). are given in Table 6. One can see that the effect of temperature on size parameters was significant. Consequently, they were independent of addition of sugars. Table 6 shows that, on increasing the temperature from 30 to 60°C, the semiminor axis remains almost constant (~26 Å), whereas semimajor axis increased by 2.5-foldand N_{agg} increased by threefold. This indicated a twofold lateral association at 45°C and a threefold association at 60°C. The micelles were ellipsoid at 30°C; however, they likely aggregated laterally and becoming rodlike with double and triple aggregation number. The N_{agg} were high (8); however, there may have been some voids in the micelle structure. Higher temperature may have caused more voids. Hence, the arrangement of the molecules in the micelle was not compact bur rather loose, with consequent voids. The formation of micelle in presence of sugars was therefore reasonably complex. In the presence of D-glucose at different temperatures, both the axial ratio as well as N_{agg} were different from those of pure $C_{12}E_{10,}$ indicating that sugar molecules interfered with micelle formation, probably by being at the micelle-water interface.

The axial ratio and N_{agg} increased when the concentration of D-glucose was incresed. At the same concentration (0.3M), N_{agg} was not significantly affected by any additive and was the same as forpure $C_{12}E_{10.}$ whereas the axial ratio remained more or less constant. The micellar growth in both size and N_{agg} also was observed by Kumar *et al.* (30). They observed the effect of quaternary ammonium bromide, R_4NBr on sodium dodecyl sulfate (SDS) micelle and found that N_{agg} of 0.3M SDS in 0.3 M C_4H_9NBr give 340, with axial ratio 6.06. Robson and Dennis (33) investigated the geometry of nonionic surfactant Triton X-100 by intrinsic viscosity and by SANS studies and showed that TX-100 formed both oblate and prolate ellipsoid micelles. We also find oblate ellipsoid micelle at 30°C which become prolate ellipsoid (or rod) at 60°C. Recently Pal *et al.* (50) analyzed the effect of hydrotopes on CTAB micelle by SANS and viscosity, and observed that N_{agg} >500 with axial ratio of >7. The authors concluded that the micellar shape changed from spherical to ellipsoidal depending upon the additive.

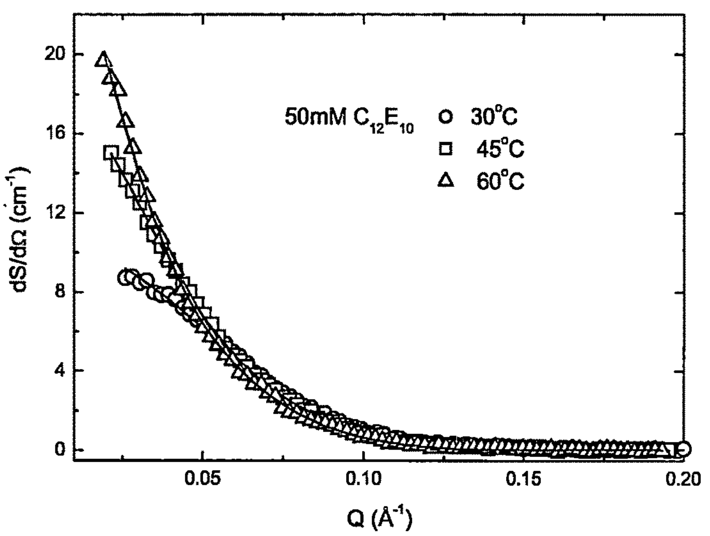

Figure 3. SANS distribution for 50mM $C_{12}E_{10}$ at different temperatures, solid line are theoretical fits, symbols are experiment values.

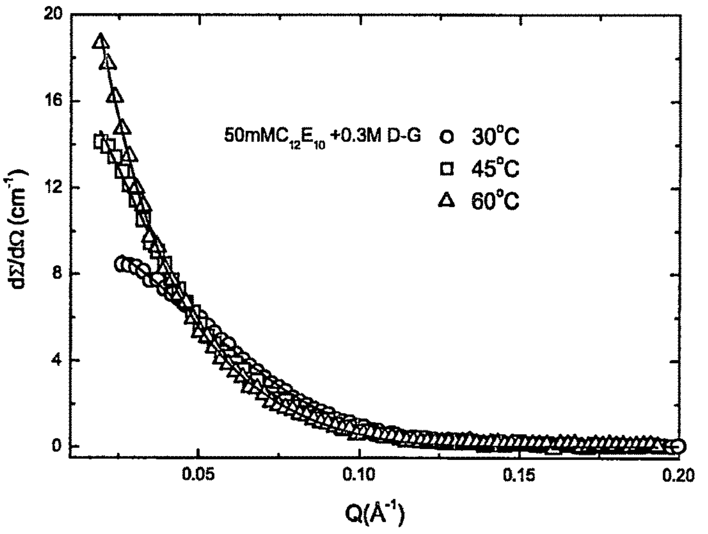

Figure 4. SANS distribution for 50mM $C_{12}E_{10}$ in presence of 0.3M D-glucose at different temperatures, solid line are theoretical fits, symbols are experiment values.

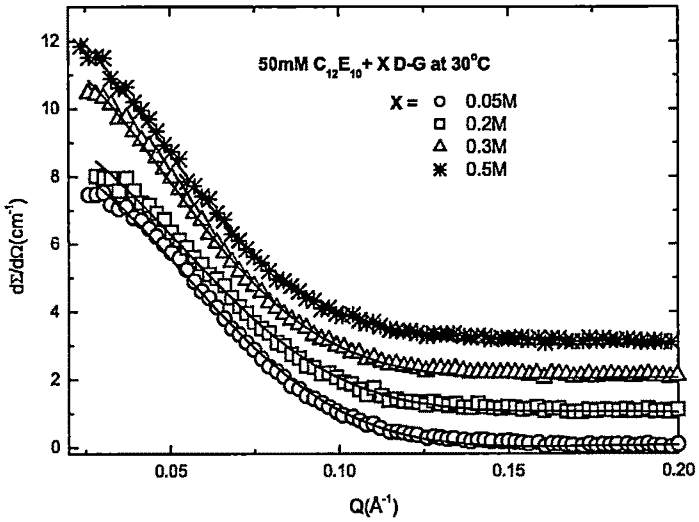

Figure 5. SANS distribution for 50mM $C_{12}E_{10}$ in presence of D-glucose at different concentration at 30°C, solid line are theoretical fits, symbols are experiment values. Distributions are shifted by 0,1,2,3 units in vertical direction respectively.

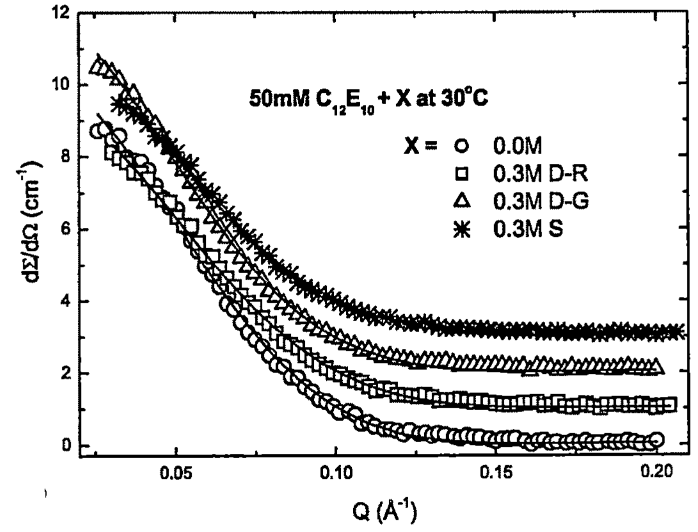

Figure 6. SANS distribution for 50mM $C_{12}E_{10}$ in presence of D-ribose, D-glucose and sucrose at 30°C, solid line are theoretical fits, symbols are experiment values. Distributions are shifted by 0,1,2,3 units in vertical direction respectively.

TABLE 6. Micellar parameters of 50mM $C_{12}E_{10}$ at Different Temperatures and in presence of sugars.

Micellar System $C_{12}E_{10}$ Temp (°C)	Semimajor axis a (Å)	Semiminor axis b=c (Å)	Axial ratio a/b	Aggregation number N_{agg}	Micellar density N_m ($cm^{-3} \times 10^{16}$)
30	41.5 ±2.1	26.8 ±1.3	1.5 ±0.08	327 ±16	9.2 ±0.46
45	72.2 ±3.6	26.6 ±1.3	2.7 ±0.14	551 ±28	5.5 ±0.28
60	101.1 ±5.1	28.9 ±1.4	3.5 ±0.18	895 ±45	3.4 ±0.17
$C_{12}E_{10}$+ 0.3M D-G					
30	44.5 ±2.2	26.2 ±1.3	1.7 ±0.09	336 ±17	8.9 ±0.45
45	80.5 ±4.0	26.9 ±1.3	3.0 ±0.15	629 ±31	4.8 ±0.24
60	122.9 ±6.1	28.6 ±1.4	4.3 ±0.22	1066 ±53	2.8 ±0.14
$C_{12}E_{10}$+ D-G (M) At 30°C					
0.05	31.1 ±1.6	26.6 ±1.3	1.2 ±0.06	242 ± 12	12.4 ±0.62
0.2	37.9 ±1.9	26.4 ±1.3	1.4 ±0.07	290 ±15	10.4 ±0.52
0.3	44.5 ±2.2	26.2 ±1.3	1.7 ±0.09	336 ±17	8.9 ±0.45
0.5	48.7 ±2.4	25.2 ± 1.3	1.9 ±0.10	340 ±17	8.9 ±0.45
$C_{12}E_{10}$+0.3M Sugar At 30°C					
D-R	41.7 ±2.1	25.2 ±1.3	1.7 ±0.09	291 ±15	10.3 ±0.52
D-G	44.5 ±2.2	26.2 ±1.3	1.7 ±0.09	336 ±17	8.9 ±0.45
Sucrose	43.1 ±2.2	24.6 ±1.2	1.8 ±0.09	287 ±14	10.5 ±0.53

As illustrated in Figure 3 and 4, no correlation peak were observed in the low (upto 0.025) *Q* region, but absolute intensities were increased by *ca.*1.5 times at high temperatures, showing the absence of spatial correlation among the nearest neighbors. A rise in temperature results in the dehydration of both the core and corona of the aggregates, and thereby systematically elongating the semimajor axis (*a*), increasing the aggregation number, and even decreases the N_m of the micelle. A look at column six in Table 6 reveals that the elongation along the major axis of the aggregates systematically increased the $N_{agg,}$ at elevated temperatures, both in the presence and in the absence of sugars. The increase in the N_{agg} suggests that more surfactant molecules had been added into the space created by the expulsion of water, probably from the core and corona portion of the micelles. The increase in size of the micelles should decrease the number density of aggregates in unit volume (N_m), which was also observed.

Cloud Point

CP is the manifestation of the solvation / desolvation phenomena in nonionic surfactant solution. The desolvation of the hydrophilic group of the surfactant leads to the formation of clouding. All three sugars studied decrease the CP of $C_{12}E_{10}$ (Figure 7).

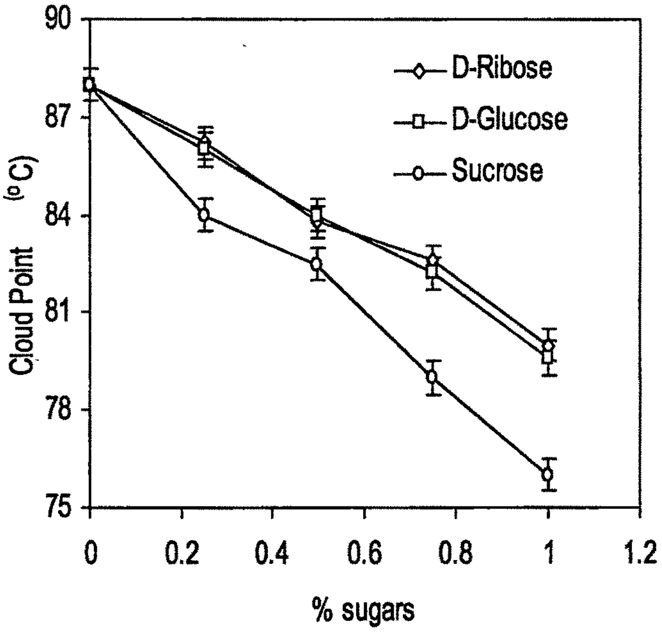

Figure 7. Variation of Cloud point of $C_{12}E_{10}$ (1%) with weight % of sugars.

As earlier mentioned, sugars can form structured solvent, and sucrose is probably better structure maker than ribose and glucose because it has more hydroxyl groups. This suggests that, in its presence, there are fewer water molecules surrounding the micelle and, consequently, it is easier for the micelles to approach each other. The CP of $C_{12}E_{10}$ (1% wt/vol) is 88°C (11). We have not studied the system by the SANS and viscosity around this temperature.

Viscosity

The intrinsic viscosity $|\eta|$ decreased with an increase in temperature, indicating pronounced micellar dehydration (Table 7). That the viscosity of a liquid decreases with rise in temperature is well known. An increasing random movement of solute surfactant molecules also occurs on increasing the temperature because of the increasing in kinetic energy. The micelles become compact with an increase in temperature owing to dehydration of OE chains. In presence of sugars similar behavior has been observed with respect to temperature. However, $|\eta|$ increase because of co-solubilization when the concentration of sugars is increased. Among the sugars considered, the variation is in the order of: sucrose > D-glucose > D-ribose.

TABLE 7 Rheological parameters of 50mM $C_{12}E_{10}$ at different temperature and in presence of sugars.

Micellar System Temp (°C)	$|\eta|$ (cm^3/g)	V_h ($x10^4 Å^3$)	V_c ($x10^4 Å^3$)	V_{OE} ($x10^4 Å^3$)	V_{OE}/V_h
30	6.60	89.7	12.5	77.2	0.94
45	6.02	137.9	21.4	116.5	0.84
60	3.99	148.5	35.4	113.1	0.76
$C_{12}E_{10}$+0.3M D-G					
30	10.67	149.9	12.8	136.2	0.91
45	9.83	257.1	24.4	232.6	0.91
60	9.13	404.6	42.1	362.5	0.90
$C_{12}E_{10}$+ D-G At 30°C					
0.05M	7.12	71.6	9.23	62.4	0.87
0.2M	8.63	104.1	11.1	93.0	0.89
0.3M	10.67	149.9	12.8	136.2	0.91
0.5M	14.38	203.2	13.0	190.3	0.94
$C_{12}E_{10}$+0.3M Sugars At 30°C					
D-R	9.19	111.8	11.1	100.7	0.90
D-G	10.67	149.1	12.8	136.3	0.91
Sucrose	16.60	198.1	11.0	187.1	0.94

(The error in the data is <5%)

The hydrated micellar volume (V_h) were computed from the intrinsic viscosity by the relation $V_h=|\eta|\ Mm/2.5N_A$, where M_m ($=A_{agg}\ M$) is the micellar molecular weight, A_{agg} is the aggregation number obtained by SANS studies (taken from Table 6) and M is the molecular weight of $C_{12}E_{10}$. The volume of the hydrocarbon core (V_c) and the volume of the palisade layer of ethylene oxide units (V_{OE}) were calculated using the following equations (10):

$$V_c = A_n V = 10^{24} A_n M_c / dN \qquad [13]$$

and

$$V_{OE} = V_h - V_c \qquad [14]$$

where V is the volume of alkyl chain length in a single $C_{12}E_n$ molecule, M_c is the molecular weight (170) and d is the density of the corresponding liquid n-alkane at different temperatures, as mentioned earlier. The calculations for several systems on which SANS studies were performed are presented in Table 7. The V_h, V_c and V_{OE} units increased as the concentration of D-glucose increased (Table 7). This may have resulted from the interaction of the OH moiety of sugars interacting with the OE part of nonionic surfactant at the micelle-water interface. Both V_h and V_{OE} increased as temperature increased. This occurred because the N_{agg} of the micelle increased, which we attributed to a lateral joining of the micelles. Obviously, with an increase in temperature, V_c should increase, and that was observed. The variation in V_{OE}/V_h ratio with temperature was a function of size and nature of the additive.

The thermodynamic activation parameters for the viscous flow were evaluated by using the Frenkel-Eyring equation (51)

$$\ln(\eta V / Nh) = \frac{\Delta H^{\#}_{vis}}{RT} - \frac{\Delta S^{\#}_{vis}}{R} \qquad [15]$$

where V, N, h and R are the molar volumes, Avogadro number, Plank's constant and the universal gas constant, respectively. From the slope and the intercepts of the straight line obtained by plotting $\ln(\eta V/Nh)$ against 1/T, the activation enthalpy ($\Delta H^{\#}_{vis}$) and activation entropy ($\Delta S^{\#}_{vis}$) for a viscous flow were calculated.

All the thermodynamic activation parameters for the system are presented in Table 8. $\Delta G^{\#}_{vis}$ was positive in all these systems, indicating a nonspontaneous flow, and it increased with an increased in the concentration of sugars in the order of: sucrose > glucose > ribose. $\Delta H^{\#}_{vis}$ value indicated that the viscous flow were endothermic. $\Delta S^{\#}_{vis}$ were positive indicating that the micellar system were not very well structured, either in the absence or presence of sugars.

TABLE 8. Thermodynamic Activation Parameters of Viscous Flow of Decaoxyethylene n-dodecyl ether ($C_{12}E_{10}$, 50mM) in the Presence of sugar.

Conc. of sugar (M) D-ribose	$\Delta G^{\#}_{vis}$ (kJmol^{-1}) at 45°C	$\Delta H^{\#}_{vis}$ (kJmol^{-1})	$\Delta S^{\#}_{vis}$ (Jmol^{-1}K^{-1})
0.0	9.15	16.9	24.3
0.1	9.23	16.1	21.5
0.3	9.37	15.5	19.3
0.5	9.46	15.5	19.1
D-glucose			
0.1	9.26	15.8	20.6
0.3	9.45	15.8	20.0
0.5	9.67	15.8	19.3
sucrose			
0.1	9.37	15.8	20.2
0.3	9.76	16.6	21.6
0.5	10.2	17.5	22.7

(The error in the data is <5%)

NMR measurement

The ^{1}H NMR spectroscopy study of the micellar rich solution in the presence of sugars was conducted to determine the electronic atmosphere around the protons and the additive effects on the atmosphere. Peak assignments were calculated for CH_3-$C_\beta H_2$-$(CH_2)_n$-$C_\alpha H_2$-$(OCH_2CH_2)_{10}$-OH (9,52) with the 3.69 ppm peak corresponding to the OE $(OCH_2CH_2)_m$ moiety, 3.45 for $C_\alpha H_2$, 1.57 for $C_\beta H_2$, 0.88 for CH_3 and 1.29 ppm peak for methylene protons $(CH_2)_n$. The changes in chemical shifts attributable to the addition of sugars were monitored and the change in chemical shift of OE units was downfield from 3.69 to 3.71ppm. This result shows that these hydrophilic molecules were interacting with micelle through intermolecular hydrogen bonding. The extent of intermolecular H-bonding was decreased by dilution with a nonpolar solvent and with an increase in temperature. This effect was seen in viscosity data. No change was observed in the chemical shift of the sugar proton. These results show that surfactant aggregates grow in size. The main OE signals become broader and spitted when the sugars were added in a 1:1 ratio. The NMR results suggests that the sugars were affecting the hydrophilic group, i.e., OCH_2 CH_2, by interacting with it, probably at the micelle-water interface and that the electronic atmosphere of the OE group at the interface was also affected, but not strongly.

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