CHAPTER - 3

PHYSICOCHEMICAL STUDIES OF PURE AND MIXED SURFACTANT SYSTEMS

3.1 Preview

3.2 Results and Discussion

- (a) Critical Micelle Concentration (CMC)
- (b) Thermodynamics of Micellization
- (c) Adsorption Parameters
- (d) Thermodynamics of Adsorption
- (e) Cloud Point
- (f) Micellar Aggregation Number (N_{agg})
- (g) Interaction Parameter (β)
- (h) Partition Coefficients
- (i) NMR Spectroscopy

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3.1 PREVIEW

In last few years, extensive structural, kinetics and thermodynamic studies have been performed on surfactant-water systems[36,53] including the effect of additives on micellization process. The micelle formation by ionic, nonionic or mixed surfactants is a well established fact and the thermodynamic data for the micellization process under varying conditions are required in order to understand the phenomenon.

As mentioned earlier, the aggregation and surface properties of surfactants are very sensitive to temperature, pH, additives, pressure etc. Hence, the studies of the effect of various additives on the aggregational and other physicochemical properties of surfactants are of both fundamental and of practical interest. Because of the present day importance of surfactants and their mixtures in industry and in understanding the micellization process, as well as in pursuance of our own intense interest[81-83,85,86, 284,290-293] in these type of compounds, we studied the effect of additives such as PEG 400, sucrose and urea on Myrj 45, $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixed surfactant systems.

The physicochemical characterization involves the CMC determination by surface tension, conductance and iodine solubilization method, the degree of ionization of the micelle (α), the standard thermodynamic parameters of micellization such as free energy (ΔG°_m), enthalpy (ΔH°_m) and entropy (ΔS°_m) were computed from the CMC data at various temperatures. The surface tension data was used to determine the interfacial parameters like the maximum surface excess (Γ_{max}), minimum area per molecule (A_{min}) and standard thermodynamic parameters of adsorption i.e. ΔG°_{ad}, ΔH°_{ad} and ΔS°_{ad}. The micellar aggregation number (N_{agg}) for pure SDBS, $C_{12}E_{10}$ and

SDBS / $C_{12}E_{10}$ mixed system in presence of additives were determined by fluorescence measurements.

The interaction between the surfactant molecules in the mixed micelle (β^m) in presence and absence of additives for SDBS/$C_{12}E_{10}$ mixed systems was computed using Rubingh's approach. ^{1}H NMR spectroscopy was also used to study the SDBS/$C_{12}E_{10}$ mixed surfactant behavior from changes in chemical shifts and spin lattice relaxation time (T_1) for $C_{12}E_{10}$ on the addition of SDBS. In this chapter, all the physicochemical parameters determined for different systems studied are reported and the results are discussed in detail.

3.2 RESULTS AND DISCUSSION

a) Critical Micelle Concentrations :

The CMC's of polyoxyethylene (8) monostearate (Myrj 45) and polyoxyethylene (10) lauryl ether ($C_{12}E_{10}$) are given in Tables 1-3. The CMC determination was carried out to be by iodine solubilization method for Myrj 45. The property of iodine ~~being~~ an electron acceptor, able to complex with nonionic surfactants has been well recognized and hence used for the determination of CMC of nonionic surfactants[283]. The CMC was determined at different temperatures 35, 40, 45 and 50°C in presence of cosolvents PEG 400, sucrose, urea and acetamide.

However, the critical micelle concentration (CMC) of $C_{12}E_{10}$ nonionic surfactant was determined by surface tension method using du Nuoy tensiometer. Even in the case of Myrj 45 in some systems the CMC was determined by surface tension method to compare the values by both the measurements and to exclude the interference due to the possible interaction of iodine with the additives.

As observed from the Tables 1-3 in the absence of any additives, values of the CMC decreased with increasing temperature. This was observed earlier also and may be taken as a typical characteristic of a nonionic surfactant[103] within the limited range of

Table 1 : CMC values for Myrj 45 in aqueous solution in the presence of PEG 400, sucrose and urea at different temperatures (CMC in mM):

Conc. of Additive % (w/v)	**PEG 400**				**SUCROSE**				**UREA**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	0.286	0.245	0.202	0.157	--	--	--	--	--	--	--	--
0.05	0.255	0.270	0.286	0.305	0.233	0.276	0.305	0.321	0.295	0.308	0.317	0.330
0.1	0.264	0.273	0.289	0.302	0.236	0.273	0.308	0.317	0.298	0.311	0.321	0.330
0.3	0.286	0.305	0.324	0.333	0.236	0.273	0.305	0.317	0.302	0.314	0.327	0.333
0.5	0.160	0.169	0.179	0.185	0.245	0.279	0.308	0.327	0.305	0.317	0.330	0.336
0.7	0.273	0.298	0.321	0.330	0.292	0.308	0.321	0.339	0.308	0.324	0.333	0.339
1.0	0.192	0.207	0.223	0.236	0.314	0.333	0.352	0.365	0.314	0.327	0.336	0.343

Table 2 : CMC values for Myrj 45 in aqueous solution in presence of acetamide at different temperatures :

Conc. of Acetamide % (w/v)	**CMC, mM**			
	35°C	**40°C**	**45°C**	**50°C**
0.0	0.286	0.245	0.202	0.157
0.005	0.283	0.302	0.314	0.330
0.01	--	0.321	0.327	0.333
0.05	0.308	0.324	0.333	0.333
0.1	0.279	0.277	0.281	0.286
0.3	0.311	0.317	0.333	0.336
0.5	0.311	0.314	0.333	0.336
0.7	0.311	0.314	0.327	0.333
1.0	0.308	0.318	0.327	0.333

Table 3 : CMC values for polyoxyethylene (10) lauryl ether ($C_{12}E_{10}$) in aqueous solution in the presence of PEG 400, sucrose and urea at different temperatures (CMC in µM) :

Conc. of Additive % (w/v)	PEG 400				SUCROSE				UREA			
	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C
0.0	11.8	10.0	8.9	7.1	--	--	--	--	--	--	--	--
0.05	5.6	7.9	8.0	8.4	5.5	6.6	7.6	8.3	--	--	--	--
0.1	5.7	7.1	8.0	8.2	5.9	6.8	7.4	8.3	12.6	12.9	13.2	13.5
0.3	5.5	6.6	7.4	8.0	6.4	7.1	7.9	8.5	13.3	13.8	14.4	14.8
0.5	5.7	6.9	7.8	8.3	6.6	7.6	8.1	8.9	13.9	14.1	14.9	15.5
0.7	5.6	7.1	7.9	8.4	6.8	7.8	8.3	9.1	14.1	14.8	15.1	15.7
1.0	5.9	6.5	7.6	8.5	6.8	7.6	8.5	9.3	--	--	--	--

temperature studied. This lowering of CMC with increase in temperature can be ascribed to various factors such as breaking of water structure, formation of icebergs of water surrounding the solute and the presence of cloud point due to the dehydration of polyoxyethylene moiety of the surfactant molecule[103].

However, in the presence of additives this characteristic does not seem to hold good particularly so in structure forming additives like PEG 400 and sucrose. The CMC increases with increase in temperature in presence of additives which is general characteristics of ionic surfactants[294]. Nevertheless the presence of PEG 400 and sucrose significantly lowers the CMC of the surfactant.

The formation of micelle is the result of hydrophobic interaction[295]. It is well known that the London dispersion force is the main attractive force helping in the micelle formation[23]. The micellization process was significantly altered in the presence of additives molecules. It is well known that additives break the three dimensional water matrix. Moreover, there will be a formation of structure between the free water molecules and the additives, particularly those having hydrogen bond forming groups i.e. structure formers thereby promote the water structure. The hydrophobic group of the surfactant also promotes the water structure. This leads to a decrease in the CMC of Myrj 45 and $C_{12}E_{10}$ in presence of PEG 400 and sucrose.

It is to be noted that although the CMC decreased initially at all temperatures, as the concentration of the additive was increased the CMC also increased gradually. On the addition of first aliquot of both PEG 400 and sucrose the system becomes less structured than water and the CMC decreases. Further addition of additives provides a greater possibility of hydrogen bonding and the system becomes relatively more structured and CMC increases. However, it should be stressed that the CMC values obtained for Myrj 45 in presence of 0.5, 0.7 and 1.0% PEG 400 are quite unexpected and we have been unable to find a proper coherent explanation. The CMC was checked and rechecked and values were well reproducible within 1%.

Hence, the overall CMC observed can be ascribed to some antagonistic effects such as (i) formation of structure of water matrix due to hydrogen bonding ability of the additive. (ii) breaking of water structure by the very presence of sucrose by formation of cavity in the liquid structure[296] and the accommodation of sucrose in that cavity. (iii) cosolubilization and formation of mixed micelle. (iv) breaking of solvent structure with rise in temperature.

It has been suggested[297] that there are atleast 14 water molecules surrounding a sucrose molecule that clearly envisages a very structured matrix, but this also will be a reason for the dehydration of the polyoxyethylene moiety, the two effects being antagonistic to each other.

It is well known that urea is a water structure breaker and an effective modifier of aqueous solution properties[298]. The micellar solution properties are generally determined by the delicate balance of the hydrophobic / hydrophilic interactions of the surfactant with water, one expects that urea may have profoundly marked effect on these properties. To explain the action of urea on aqueous solutions two different mechanisms have been proposed in literature; (i) an indirect mechanism, wherein urea acts as a "water structure breaker" thereby facilitating the solvation of non-polar solutes[299,300] and (ii) a direct mechanism, whereby urea participates in the solvation of the hydrophobic solutes in water by replacing some water molecules in the hydration shell of the solutes. The indirect mechanism is widely accepted and many of the experimental results support the hypothesis that urea acts as a "water structure breaker". The CMC values of both Myrj 45 and $C_{12}E_{10}$ in presence of urea are given in Tables 1 and 3. It is observed that CMC increases with urea concentration for both the surfactants. As the water structure breaking property of urea is well known, the effects of an increase in temperature and addition of urea should be therefore similar. Such increase in CMC in presence of urea has been observed for other surfactants also. The CMC increase has been explained in terms of the enhanced solubility of surfactant hydrophobic group in presence of urea. Since, urea is known to be a strong protein denaturant and hence its demicellization property (i.e. higher CMC) is probably a manifestation of that. It has also been suggested that the monomers of the surfactants become stabilized in the aqueous urea solutions[301], therefore the micellization occurs at higher concentrations. Therefore, an interplay of various antagonistic properties like the breaking of the water structure and demicellization, monomer stability, solvation of hydrophilic groups (an increase in the CMC) actually determine the overall experimentally obtained result.

The effect of acetamide as an additive on the CMC of Myrj 45 as shown in Table 2 is similar to that of urea. However, acetamide is less interactive than urea as one NH_2 group of urea is replaced by a CH_3 group. This was earlier observed where acetamide increases the CMC of nonionic surfactant Brij 35[82]. The effect on Myrj 45 is much greater (125 μM) than in Brij 35 (19 μM) at 45°C for 1M acetamide.

Similarly, the effect of additives i.e. PEG 400, sucrose and urea on the CMC of sodium dodecyl benzene sulfonate (SDBS) at different temperatures 35, 40, 45 and 50°C were determined both by conductivity and surface tension measurements. In absence of any additives the CMC was found to increase as the temperature increases. In general for ionic surfactants a minimum in CMC at lower temperature region is always observed with subsequent increase as temperature increases. At higher temperatures the dielectric constants of the solution will decrease, resulting in greater repulsion between the ionic heads of surfactant molecules resulting in higher CMC[302].

The CMC values are reported in Table 4. The effect of temperature remains the same even in the presence of PEG 400 and sucrose. It should be noted that both these additives increase the CMC. It is well known that the micellar structure may be considered to be made up of two regions, an outer region comprising of polar head groups plus a portion of hydrocarbon chains in contact with water[303] (i.e. ionic heads fully and hydrocarbon chains to various degrees) and an inner region, the hydrocarbon core containing only all the remaining hydrocarbon chains not in contact with water.

Table 4 : CMC values for sodium dodecyl benzene sulfonate (SDBS) in aqueous solution in presence of PEG 400, sucrose and urea at different temperatures (CMC in mM) :

Conc. of Additive % (w/v)	PEG 400				SUCROSE				UREA			
	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C
0.0	1.99	2.32	2.64	3.02	--	--	--	--	--	--	--	--
0.1	2.06	2.42	2.82	3.08	2.12	2.46	2.76	3.08	2.17	2.46	2.72	3.10
0.3	2.18	2.46	2.94	3.12	2.14	2.46	2.83	3.12	2.20	2.48	2.82	3.14
0.5	2.26	2.44	2.96	3.18	2.20	2.52	2.88	3.14	2.24	2.52	2.94	3.16
0.7	2.28	2.52	3.02	3.24	2.55	3.00	3.18	2.34	2.54	2.98	3.19	3.19

The strong hydrogen bonding interactions of water with both PEG 400 and sucrose due to the presence of -OH groups have major effect on the water at micellar hydrocarbon-water interface, which is otherwise structured by hydrophobic effect. i.e. the structured water around the hydrophobic group is disrupted, leading to poorer contribution to the hydrophobic interactions which is the driving force for micellization, hence higher the CMC.

It is also observed from Table 4 that urea increased the CMC of sodium dodecyl benzene sulfonate (SDBS). Recently, Wang et al.[97] have investigated the effect of urea on the microenvironmental properties of SDBS micellar solutions by ESR spectroscopy and surface tension measurements at air / water interface. They also report an increase in the CMC of SDBS on addition of urea which is also observed in our results ~~too~~ attributed to the mechanism wherein urea molecules replace some water molecules that solvate the hydrophobic chain and the polar head group of the surfactant.

The critical micelle concentration (CMC) was also determined for SDBS / $C_{12}E_{10}$ mixed system at various mole ratios (9:1, 7:3, 5:5, 3:7 and 1:9) at different temperatures by both surface tension and conductivity measurements. The CMC values are given in Table 5. As expected the decreases in CMC for $C_{12}E_{10}$ and increase in case of SDBS were observed with increasing temperature[16]. However, in their mixtures the CMC is found to increase with rise in temperature indicating that mixed micelles are ionic in nature[304].

A similar study was carried out to determine the effect of various concentrations of PEG 400, sucrose and urea at different mole ratios of SDBS / $C_{12}E_{10}$ (1:9, 5:5 and 9:1) at different temperatures. The CMC values are shown in Tables 6-8. In the presence of PEG 400, sucrose as well as urea, at all the mole ratios of SDBS / $C_{12}E_{10}$ studied, the CMC was found to increase with increasing concentration of the additives. The CMC was determined by both surface tension and conductivity how was this calculated ?

Table 5 : The critical micelle concentrations (CMC) and degree of ionization (α)* for SDBS / $C_{12}E_{10}$ systems in aqueous solutions at different temperatures :

SDBS / $C_{12}E_{10}$	**CMC, mM**			
	35°C	**40°C**	**45°C**	**50°C**
10:0	1.99 (0.68)	2.34 (0.69)	2.69 (0.70)	3.02 (0.71)
9:1	0.0237 (0.59)	0.0234 (0.59)	0.0258 (0.60)	0.0268 (0.60)
7:3	0.0214 (0.052)	0.0255 (0.52)	0.0236 (0.52)	0.0247 (0.52)
5:5	0.0206 (0.50)	0.0214 (0.50)	0.0224 (0.50)	0.0234 (0.50)
3:7	0.0172 (0.42)	0.0184 (0.42)	0.0190 (0.43)	0.0202 (0.43)
1:9	0.0132 (0.39)	0.0144 (0.39)	0.0155 (0.39)	0.0162 (0.40)
0:10	0.0118	0.0100	0.0089	0.0071

* The values in the parenthesis are the degree of ionization of the micelle.

Table 6 : CMC values for SDBS/$C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of PEG 400, sucrose and urea at different temperatures (CMC in mM) :

Conc. of Additive % (w/v)	**PEG 400**				**SUCROSE**				**UREA**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	0.0132	0.0144	0.0158	0.0168	--	--	--	--	--	--	--	--
0.1	0.0150	0.0158	0.0166	0.0174	0.0142	0.0156	0.0164	0.0170	0.0154	0.0162	0.0170	0.0182
0.3	0.0154	0.0162	0.0170	0.0178	0.0148	0.0153	0.0162	0.0174	0.0158	0.0168	0.0176	0.0188
0.5	0.0158	0.0166	0.0174	0.0180	0.0152	0.0164	0.0173	0.0186	0.0162	0.0172	0.0184	0.0196
0.7	0.0162	0.0170	0.0176	0.0182	0.0156	0.0168	0.0178	0.0191	0.0166	0.0176	0.0190	0.0202

Table 7 : CMC values for SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous solution in presence of PEG 400, sucrose and urea at different temperatures (CMC in mM) :

Conc. of Additive % (w/v)	**PEG 400**				**SUCROSE**				**UREA**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	0.0206	0.0214	0.0224	0.0234	--	--	--	--	--	--	--	--
0.1	0.0210	0.0218	0.0228	0.0236	0.0208	0.0212	0.0226	0.0238	0.0212	0.0218	0.0228	0.0240
0.3	0.0212	0.0220	0.0232	0.0240	0.0210	0.0218	0.0230	0.0242	0.0216	0.0224	0.0236	0.0245
0.5	0.0218	0.0224	0.0234	0.0246	0.0218	0.0226	0.0238	0.0248	0.0220	0.0226	0.0238	0.0248
0.7	0.0220	0.0228	0.0238	0.0250	0.0220	0.0231	0.0242	0.0250	0.0225	0.0238	0.0244	0.0252

Table 8 : CMC values for SDBS / $C_{12}E_{10}$ (9:1) mixed system in aqueous solution in presence of PEG 400, sucrose and urea at different temperatures (CMC in mM) :

Conc. of Additive % (w/v)	PEG 400				SUCROSE				UREA			
	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C
0.0	0.0237	0.0248	0.0258	0.0268	--	--	--	--	--	--	--	--
0.1	0.0250	0.0262	0.0272	0.0284	0.0246	0.0252	0.0264	0.0276	0.0250	0.0262	0.0274	0.0282
0.3	0.0256	0.0264	0.0274	0.0286	0.0252	0.0264	0.0274	0.0286	0.0262	0.0274	0.0286	0.0298
0.5	0.0260	0.0272	0.0282	0.0292	0.0262	0.0276	0.0284	0.0292	0.0272	0.0284	0.0296	0.0308
0.7	0.0268	0.0276	0.0288	0.0296	0.0275	0.0284	0.0294	0.0302	0.0292	0.0301	0.0314	0.0325

methods. The overall results observed can be attributed to various antagonistic factors such as (a) breaking of water matrix by the additives; (b) formation of structure in the solvent due to hydrogen bonding; (c) electrostatic repulsions between the ionic species in presence of these additives.

b) Thermodynamics of Micellization :

As the CMC can serve as a measure of micelle stability in a given state, the thermodynamic parameters of micellization can be determined from the temperature dependence of the CMC[305]. The standard free energy of micellization (ΔG°_m) for a nonionic surfactant is directly proportional to CMC (CMC is in mole fraction scale) following the relation[16].

$$\Delta G^\circ_m = RT \ln CMC$$

The transfer process here indicates the formation of micelles in the solvent from the solvated free monomer of unit mole fraction. The standard thermodynamic quantities for nonionic surfactants Myrj 45 and $C_{12}E_{10}$ in presence and absence of additives are reported in Tables 9-12 and Tables 13-15 respectively. The standard free energy of micellization (ΔG°_m) was found to be negative throughout at all concentrations of the additives studied.

It can be noted from the tabulated data that in the absence of any additive, the ΔG°_m becomes more negative with increasing temperature. That is, the formation of micelles becomes relatively more spontaneous. Even in presence of additives the variation is similar though the CMC increases with temperature. This is obvious, as the change in magnitude of the logarithm of the CMC is more than compensated by the change in the value of RT. The variation in ΔG°_m with the concentration of additive was quite regular for both the systems, however, the variation in the free energy with PEG 400 in ease of Myrj 45 was very irregular. As we mentioned before, we do not have a proper explanation for this kind of behavior.

Table 9 : Thermodynamic parameters of micellization of Myrj 45 in aqueous solution in presence of PEG 400 at different concentrations :

Conc. of PEG 400 % (w/v)	$-\Delta G^\circ_m$ (kJ mol^{-1})				$-\Delta H^\circ_m$ (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})	$\Delta\Delta G^{o tr}_m$ (kJ mol^{-1}) (35°C)	$\Delta\Delta H^{o tr}$m (kJ mol^{-1})	$-\Delta\Delta C^{o tr}_{pm}$ (kJ mol^{-1} K^{-1})
	35°C	40°C	45°C	50°C					
0.0	31.2	32.1	33.2	34.3	-33.2	209	--	--	--
0.05	31.5	31.8	32.2	32.25	9.85	70	-0.3	-43.0	-0.262
0.1	31.4	31.8	32.2	32.5	7.55	77	-0.2	-40.7	-0.245
0.3	31.2	31.5	31.9	32.3	8.74	73	0.0	-41.9	0.632
0.5	32.6	33.0	33.4	33.9	8.07	80	-1.4	-41.3	0.229
0.7	31.3	31.6	31.4	32.3	10.06	69	-0.1	-43.3	0.375
1.0	32.2	32.5	32.8	33.2	11.31	68	-1.0	-44.5	0.612

Table 10 : Thermodynamic parameters of micellization of Myrj 45 in aqueous solution in presence of sucrose at different concentrations :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$-\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}$m (kJ mol^{-1})**	**$-\Delta\Delta C^{\circ tr}_{pm}$ (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**					
0.0	31.2	32.1	33.2	34.3	-33.2	209	--	--	--
0.05	31.7	31.8	32.0	32.4	17.5	46	-0.5	-50.7	1.610
0.1	31.7	31.8	32.0	32.4	17.1	47	-0.5	-50.3	1.420
0.3	31.7	31.8	32.0	32.4	16.9	48	-0.5	-50.1	1.741
0.5	31.6	31.7	32.0	32.3	15.7	51	-0.4	-48.9	1.104
0.7	31.1	31.5	31.9	32.2	7.9	75	-0.1	-41.1	-0.251
1.0	30.9	31.3	31.6	32.0	8.3	73	0.3	-41.5	0.128

Table 11 : Thermodynamic parameters of micellization of Myrj 45 in aqueous solution in presence of acetamide at different concentrations :

Conc. of Acetamide % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}$m (kJ mol^{-1})**	**$-\Delta\Delta C^{\circ tr}_{pm}$ (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**					
0.0	31.2	32.1	33.2	34.3	-33.2	209	--	--	--
0.005	31.2	31.5	31.9	32.2	8.15	75	0.0	-41.3	-0.249
0.01	--	31.4	31.8	32.2	3.2	90	--	-36.4	-0.218
0.05	31.0	31.4	31.8	32.2	4.9	85	0.2	-38.1	-0.205
0.3	31.0	31.4	31.8	32.2	4.7	85	0.2	-37.9	-0.230
0.5	31.0	31.4	31.8	32.2	5.6	82	0.2	-38.8	-0.232
0.7	31.0	31.4	31.8	32.3	4.3	87	0.2	-37.5	-0.224
1.0	31.0	31.4	31.8	32.3	4.4	86	0.2	-37.6	-0.100

Table 12 : Thermodynamic parameters of micellization of Myrj 45 in aqueous solution in presence of urea at different concentrations :

Conc. of Urea % (w/v)	$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})	ΔS°_{m} (J mol^{-1} K^{-1})	$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)	$\Delta\Delta H^{\circ tr}$m (kJ mol^{-1})	$-\Delta\Delta C^{\circ tr}_{pm}$ (kJ mol^{-1} K^{-1})
	35°C	40°C	45°C	50°C					
0.0	31.2	32.1	33.2	34.3	-33.2	209	--	--	--
0.05	31.1	31.5	31.9	32.3	5.9	82	0.1	-39.1	-0.235
0.1	31.1	31.5	31.9	32.3	5.5	83	0.1	-38.7	0.036
0.3	31.0	31.4	31.8	32.3	5.5	83	0.2	-38.7	0.172
0.5	31.1	31.4	31.8	32.3	8.0	75	0.1	-41.2	0.446
0.7	31.0	31.4	31.8	32.2	5.3	83	0.1	-38.5	0.310
1.0	30.9	31.3	31.8	32.2	4.5	86	0.3	-37.7	0.046

Table 13 : Thermodynamic parameters of micellization of $C_{12}E_{10}$ in aqueous solution in presence of PEG 400 at different concentrations :

Conc. of PEG 400 % (w/v)	**$-\Delta G^\circ_m$ (kJ mol^{-1})**				**$-\Delta H^\circ_m$ (kJ mol^{-1})**	**ΔS°_m (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{otr}_m$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{otr}m$ (kJ mol^{-1})**	**$\Delta\Delta C^{otr}_{pm}$ (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**					
0.0	39.3	40.4	41.4	42.6	-27	220	--	--	--
0.05	41.2	41.4	41.7	42.2	21	66	-1.9	-48.0	1.79
0.1	41.2	41.3	41.8	42.3	20	69	-1.9	-47.0	1.50
0.3	41.2	41.5	41.9	42.3	21	67	-2.0	-48.0	1.24
0.5	41.2	41.4	41.7	42.2	21	66	-1.9	-48.0	1.54
0.7	41.2	41.3	41.7	42.2	22	61	-1.9	-49.0	2.06
1.0	41.1	41.6	41.8	42.1	21	66	-1.8	-48.0	-0.298

The maximum error in ΔG°_m is 0.1%, in ΔH°_m is 25% and in ΔS°_m is 7%.

Table 14 : Thermodynamic parameters of micellization of $C_{12}E_{10}$ in aqueous solution in presence of sucrose at different concentrations :

Conc. of Sucrose % (w/v)	$-\Delta G^\circ_m$ (kJ mol^{-1})				$-\Delta H^\circ_m$ (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})	$\Delta\Delta G^{\circ tr}_m$ (kJ mol^{-1}) (35°C)	$\Delta\Delta H^{\circ tr}$m (kJ mol^{-1})	$\Delta\Delta C^{\circ tr}_{pm}$ (kJ mol^{-1} K^{-1})
	35°C	40°C	45°C	50°C					
0.0	39.3	40.4	41.4	42.6	-27	220	--	--	--
0.05	41.3	41.5	41.8	42.2	23	60	-2.0	-50.0	-0.316
0.1	41.1	41.4	41.9	42.2	18	76	-1.8	-45.0	-0.298
0.3	41.0	41.3	41.7	42.1	18	74	-1.7	-45.0	-0.278
0.5	40.8	41.1	41.6	42.0	15	80	-1.5	-42.0	-0.273
0.7	40.8	41.1	41.6	42.0	15	80	-1.5	-42.0	-0.273
1.0	40.8	41.1	41.5	41.9	18	74	-1.5	-45.0	-0.285

The maximum error in ΔG°_m is 0.1%, in ΔH°_m is 11% and in ΔS°_m is 7%.

Table 15 : Thermodynamic parameters of micellization of $C_{12}E_{10}$ in aqueous solution in presence of urea at different concentrations :

Conc. of Urea % (w/v)	$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})	ΔS°_{m} (J mol^{-1} K^{-1})	$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1})	$-\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})
	35°C	40°C	45°C	50°C				
0.0	39.3	40.4	41.4	42.6	-27	220	--	--
0.1	39.2	39.7	40.3	40.9	3.8	115	1.1	31.1
0.3	39.0	39.6	40.1	40.6	5.9	108	1.3	33.2
0.5	38.9	39.5	40.0	40.5	5.7	108	1.4	33.0
0.7	38.9	39.4	39.9	40.5	5.6	108	1.5	32.9

In the case of ionic and mixed (ionic / nonionic) surfactants, the standard free energy of micellization is given by[295] -

$$\Delta G^\circ_m = (2-\alpha)\, RT \ln CMC$$

α is the degree of ionization of the micelle obtained usually from the ratio of the slopes of the conductivity - concentration plots both above and below the CMC[159]. The negative ΔG°_m values observed for SDBS and SDBS / additive / water ternary (Tables 16-18) systems indicate a spontaneous micelle formation. Similar was the case in mixed SDBS / $C_{12}E_{10}$ system (Table 19). Moreover, the ΔG°_m values for the mixtures were more negative than their corresponding pure components. This suggests that mixed micelle formation is relatively more favored. As shown in Fig. 12 a minimum is observed at $N_{SDBS} = 0.1$ indicative of mixed micelle stability.

In Tables 19-28 the thermodynamic quantities for SDBS / $C_{12}E_{10}$ mixed system at mole ratios 1:9, 5:5 and 9:1 at various concentrations of different additives are given. It is observed that both in presence and absence of additives ΔG°_m becomes more negative with increase in temperature indicating that the micelle formation is favoured at higher temperature. A spontaneous mixed micelle formation is observed not only in absence but also in presence of PEG 400, sucrose and urea. However, it is observed that ΔG°_m values in absence of these additives are lower than in its presence i.e. mixed micelle formation becomes less spontaneous in presence of these additives. As the micellization process is accompanied by appreciable changes in water structure, as mentioned earlier, the changes observed in ΔG°_m may be ascribed to the pronounced effect of these additives on the water structure.

The temperature variation of the CMC can be used to compute the enthalpy of micellization ΔH°_m and hence the entropy of micellization ΔS°_m. The following relations have been used for these computations -

Table 16 : Thermodynamic parameters of micellization of sodium dodecyl benzene sulfonate (SDBS) in aqueous solution in presence of PEG 400 :

Conc. of PEG 400 % (w/v)	**$-\Delta G^\circ_m$ (kJ mol^{-1})**				**$-\Delta H^\circ_m$ (kJ mol^{-1})**	**ΔS°_m (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_m$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_m$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	34.2	34.3	34.1	33.6	46.8	-40	--	--
0.1	34.5	34.6	34.8	35.0	23.7	35	-0.3	23.1
0.3	34.5	34.7	34.9	35.0	24.2	33	-0.3	22.6
0.5	34.7	34.9	35.1	35.4	20.2	47	-0.5	26.5
0.7	34.6	34.9	35.0	35.3	20.8	45	-0.4	26.0

Table 17 : Thermodynamic parameters of micellization of sodium dodecyl benzene sulfonate (SDBS) in aqueous solution in presence of sucrose :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1})**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	34.2	34.3	34.1	33.6	46.8	-40	--	--
0.1	34.4	34.6	34.8	35.0	22.0	40	-0.2	24.8
0.3	34.3	34.7	35.0	35.2	16.2	59	-0.1	30.6
0.5	34.5	34.7	34.9	35.2	20.6	45	-0.3	26.2
0.7	34.7	34.8	35.1	35.3	22.9	38	-0.5	23.9

Table 18 : Thermodynamic parameters of micellization of sodium dodecyl benzene sulfonate (SDBS) in aqueous solution in presence of urea at different concentrations :

Conc. of PEG 400 % (w/v)	$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})	ΔS°_{m} (J mol^{-1} K^{-1})	$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1})	$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})
	35°C	40°C	45°C	50°C				
0.0	34.2	34.3	34.1	33.6	46.8	-40	--	--
0.1	34.3	34.5	34.6	34.9	23.3	36	-0.1	23.5
0.3	34.4	34.5	34.8	34.9	22.4	39	-0.2	24.4
0.5	34.5	34.6	34.9	35.2	19.6	48	-0.3	27.2
0.7	34.3	34.6	34.8	35.1	17.6	54	-0.1	29.2

Table 19 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ in aqueous solution at various mole ratios :

Conc. of PEG 400 % (w/v)	$-\Delta G^\circ_m$ (kJ mol^{-1})				$-\Delta H^\circ_m$ (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})
	35°C	40°C	45°C	50°C		
10:1	34.2	34.3	34.1	33.6	46.8	-40
9:1	53.0	53.5	53.9	54.5	22.8	98
7:3	56.0	56.7	57.4	58.1	13.1	139
5:5	57.0	57.7	58.4	59.0	15.2	136
3:7	60.6	61.2	61.8	62.5	20.7	129
1:9	63.0	63.5	64.1	64.7	29.2	110
0:10	39.3	40.4	41.3	42.6	-27.2	216

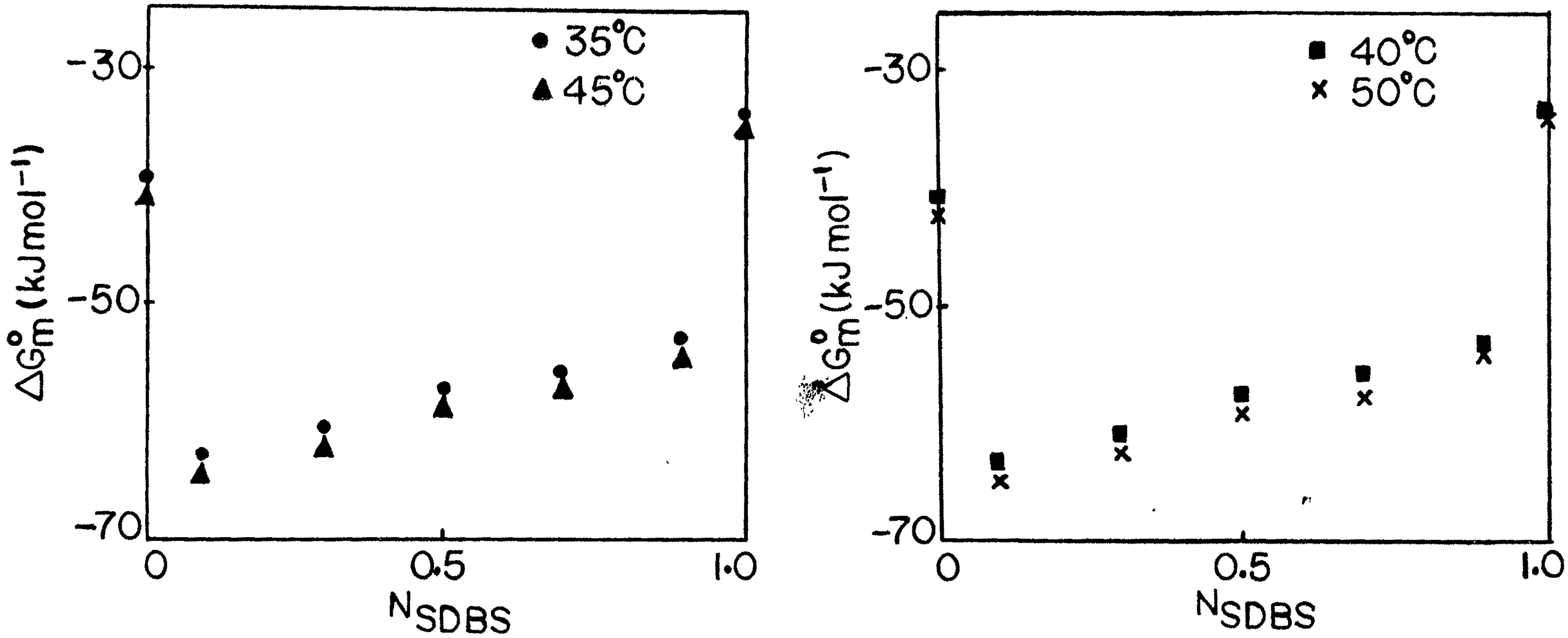

Fig. 12 : ΔG°_m - mole fraction of SDBS for SDBS / $C_{12}E_{10}$ mixed system at different temperature.

Table 20 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of PEG 400 at different concentrations :

Conc. of PEG 400 % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	63.0	63.5	64.1	64.7	29.2	110	--	--
0.1	61.4	61.8	62.2	62.5	38.9	73	1.6	-9.7
0.3	61.5	62.0	62.5	62.9	33.0	93	1.5	-3.8
0.5	61.6	62.0	62.4	62.9	34.9	87	1.4	-5.7
0.7	61.1	61.5	61.9	62.3	36.8	79	1.9	-7.6

The maximum error in ΔG°m is < 1% and that of ΔH°m is 7% and in ΔS°m is 8%.

Table 21 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of sucrose at different concentrations :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	63.0	63.5	64.1	64.7	29.2	110	--	--
0.1	60.8	61.2	61.6	61.9	36.2	80	2.2	-7.0
0.3	60.6	61.0	61.5	61.9	36.9	90	2.4	-3.7
0.5	61.2	61.5	61.9	62.4	36.3	81	1.8	-7.1
0.7	61.3	61.7	62.1	62.5	37.1	79	1.7	-7.9

Table 22 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of urea at different concentrations :

Conc. of Urea % (w/v)	**$-\Delta G°_m$ (kJ mol^{-1})**				**$-\Delta H°_m$ (kJ mol^{-1})**	**$\Delta S°_m$ (J mol^{-1} K^{-1})**	**$\Delta\Delta G°^{tr}_m$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H°^{tr}_m$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	63.0	63.5	64.1	64.7	29.2	110	--	--
0.1	60.2	60.5	60.9	61.1	41.9	60	2.8	-12.7
0.3	59.9	60.3	60.6	61.0	39.3	67	3.1	-10.1
0.5	59.6	59.9	60.2	60.4	44.3	50	3.4	-15.1
0.7	59.5	59.7	60.0	60.3	41.7	57	3.5	-12.5

Table 23 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous solution in presence of PEG 400 at different concentrations :

Conc. of PEG 400 % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	57.0	57.7	58.4	59.0	15.2	186	--	--
0.1	53.7	54.1	54.4	54.8	30.2	76	3.3	-15.0
0.3	53.5	53.9	54.2	54.5	33.0	67	3.5	-17.8
0.5	53.4	53.9	54.4	54.9	23.2	98	3.6	-8.0
0.7	53.8	54.3	54.7	55.2	24.6	95	3.2	-9.4

Table 24 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous solution in presence of sucrose at different concentrations :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	57.0	57.7	58.4	59.0	15.2	136	--	--
0.1	54.6	54.9	55.1	55.4	38.9	51	2.4	-23.7
0.3	54.8	55.0	55.4	55.7	35.5	63	2.2	-20.3
0.5	54.7	55.0	55.3	55.6	35.3	63	2.3	-20.1
0.7	54.3	54.7	54.9	55.3	34.3	65	2.7	-19.1

Table 25 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous solution in presence of urea at different concentrations :

Conc. of Urea % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	57.0	57.7	58.4	59.0	15.2	136	--	--
0.1	52.5	53.0	53.4	53.8	27.4	82	4.5	-12.2
0.3	52.3	52.7	53.1	53.5	26.6	83	4.7	-11.4
0.5	52.1	52.6	53.1	53.4	25.1	88	4.9	-9.9
0.7	52.2	52.5	52.9	53.4	27.6	80	4.8	-12.4

Table 26 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of PEG 400 at different concentrations :

Conc. of PEG 400 % (w/v)	$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})	ΔS°_{m} (J mol^{-1} K^{-1})	$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)	$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})
	35°C	40°C	45°C	50°C				
0.0	53.0	53.5	53.9	54.5	22.8	98	--	--
0.1	51.4	51.8	52.0	52.4	32.4	62	1.6	-9.6
0.3	51.8	52.0	52.4	52.7	31.8	65	1.2	-9.0
0.5	52.3	52.5	52.8	53.1	37.0	50	0.7	-14.2
0.7	51.6	51.9	52.3	52.5	33.0	59	1.4	-10.7

Table 27 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of Sucrose at different concentrations :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	53.0	53.5	53.9	54.5	22.8	98	--	--
0.1	49.1	49.3	49.6	49.9	31.9	56	3.9	-9.1
0.3	49.7	50.0	50.3	50.6	31.2	60	3.3	-8.4
0.5	49.7	50.0	50.3	50.5	33.1	54	3.3	-10.3
0.7	49.7	50.0	50.3	50.5	33.1	54	3.3	-10.3

Table 28 : Thermodynamic parameters of micellization of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous solution in presence of urea at different concentrations :

Conc. of Urea % (w/v)	**$-\Delta G^{\circ}_{m}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{m}$ (kJ mol^{-1})**	**ΔS°_{m} (J mol^{-1} K^{-1})**	**$\Delta\Delta G^{\circ tr}_{m}$ (kJ mol^{-1}) (35°C)**	**$\Delta\Delta H^{\circ tr}_{m}$ (kJ mol^{-1})**
	35°C	**40°C**	**45°C**	**50°C**				
0.0	53.0	53.5	53.9	54.5	22.8	98	--	--
0.1	49.6	49.9	50.3	50.7	26.9	74	3.4	-4.1
0.3	49.5	49.9	50.2	50.5	28.2	69	3.5	-5.4
0.5	49.7	49.9	50.2	50.5	32.3	56	3.3	-9.5
0.7	49.4	49.7	50.0	50.2	33.7	51	3.6	-10.9

$$\Delta H^\circ_m = - RT^2 \, d \ln CMC / dT$$

$$\Delta S^\circ_m = (\Delta H^\circ_m - \Delta G^\circ_m) / T$$

The data in Tables 9-12 and 13-15 for Myrj 45 and $C_{12}E_{10}$ in absence of any additive indicate that the micellization process was endothermic although it becomes exothermic in presence of additives. This has been earlier observed by us for Triton X 100 - PEG 400 systems, although the micellization process was endothermic in case of Brij 35 for most of the additive concentrations. The exothermic and endothermic characteristics of micellization are specific to the surfactant, additive and temperature. It should also be mentioned here that the ΔH°_m values calculated from the above equation may be somewhat different from the calorimetrically determined data. The calorimetric data are in general scarce, and we have been unable to locate any for our system for comparison. It has been mentioned earlier[162] that the ΔH°_m for nonionic surfactant is independent of number of oxyethylene groups when the number is over six and the value is ~ 32 kJ mol^{-1}. For Myrj 45 and $C_{12}E_{10}$ ~ 33 kJ mol^{-1} and ~ 28 kJ mol^{-1} respectively were obtained at 20°C. The ΔH°_m values are almost independent of temperature in presence of additives for both the nonionic surfactant systems.

For SDBS and mixed SDBS / $C_{12}E_{10}$ systems both in presence and absence of additives, the enthalpy of micellization ΔH°_m was computed from ΔG°_m - T plots using well known relation -

$$\Delta G^\circ_m = \Delta H^\circ_m - T \, \Delta S^\circ_m$$

In all the SDBS systems, for SDBS / $C_{12}E_{10}$ mixed system the micellization process was exothermic. Similar exothermic contribution was observed for mixed systems in presence of PEG 400, sucrose and urea, ΔH°_m was again a temperature independent quantity. The overall independence in ΔH°_m can be attributed to the fact that there does not occur a remarkable change in the environment surrounding the hydrocarbon chain of the surfactant molecule in presence of additives as the temperature is changed. Also, with increasing concentrations of additives ΔH°_m does not change much which indicates that the environment surrounding the surfactant molecules does not vary much with further addition of amounts of additives. However, this independence may also be due to the error associated with ΔH°_m as the error in ΔH°_m is in the range of ± 10%.

The entropy of micellization (ΔS°_m) is positive for all the systems studied both in presence and absence of additives. This suggests that the micellization process is somewhat entropy dominated particularly for systems where entropy changes are very high[83]. High entropy changes are generally associated with phase change. Hence, it can be assumed that micelles are separate phase in these systems. Shaw[1] has suggested that the high entropy changes may be due to greater freedom of movement of the hydrocarbon chains in the micellar core. However, it is not clear how this movement of hydrocarbon chains in the core of the micellar aggregates can have a dominating effect on ΔS°_m, which is a macroscopic property. Rosen[29] has stated that the presence of the hydrated oxyethylene groups of the surfactant introduces structure in the liquid water phase and that the removal of the surfactant via micellization results in an increase in the overall randomness and hence increase in entropy. It is to be noted that in aqueous systems in absence of any additive a positive ΔH°_m and negative ΔG°_m leads to large positive entropy. In the presence of additives, the entropy changes are not very large because the additives still control the formation of three dimensional water structure.

The hydrophobic effect due to the interaction between the hydrocarbon tail of the surfactant and water plays an important role in the micelle formation. According to Lumry and Rajender[306] for a compensation phenomenon, the micellization can be described as consisting of two processes (i) the 'desolvation' i.e. the dehydration of the hydrocarbon tail of the surfactant molecules and (ii) the 'chemical' part i.e. the aggregation of the tails of the surfactant molecules to form micelles. In general, the compensation phenomenon between the enthalpy change, ΔH°_{m} and the entropy change ΔS°_{m} in various processes can be written as follows -

$$\Delta H^{\circ}_{m} = k_1 + k_2\, \Delta S^{\circ}_{m}$$

From the thermodynamics, $\Delta G^{\circ}_{m} = \Delta H^{\circ}_{m} - T\Delta S^{\circ}_{m}$

therefore by substituting for ΔH°_{m} in the general thermodynamic relation.

$$\Delta G^{\circ}_{m} = k_1 + (k_2 - T)\, \Delta S^{\circ}_{m}$$

where k_2 is the isostructural temperature i.e. the slope of ΔH°_{m} Vs ΔS°_{m} plot, T is the absolute temperature. It was suggested by Lumry et al.[306] that the value for water was expected to be between 270-294 K. As shown in Fig. 13-16 the values obtained for Myrj 45, $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixed system fall within this range. Although, it should be noted that for SDBS / $C_{12}E_{10}$ mixed system in absence of additives, not a very good correlation was observed ($r = 0.97$). Such enthalpy entropy composition have been observed for many physicochemical processes including micellization and monolayer formation[307]. The small variation that we observe here as well as those observed earlier may be due to the difference in the bulk structural property of the solution from that of water. The isostructural temperature has a thermodynamic significance. It can be interpreted as a characteristic of solute-solute and solute-solvent interactions i.e. proposed as a measure of the "desolvation" part of micellization process, whereas the intercept, k_1 characterizes the solute-solute interaction i.e. considered as index of the "chemical" part of the micellization process. Hence, the intercept represents the enthalpy effect under the condition ΔS°_{m}=O i.e. $\Delta G^{\circ}_{m} = k_1$ (At the isostructural temperature, the micellization process is totally independent of any structural change in the system)..The increase in the intercept, k_1, corresponds to a decrease in the stability of the structure of micelles[308].

The ΔH°_{m} - ΔS°_{m} compensation plot as shown in Fig. 16 for SDBS / $C_{12}E_{10}$ mixtures in presence of additives PEG 400, sucrose and urea shows that although the slope value is same i.e. 285 K for 1:9, 5:5 and 9:1 mole ratios the intercept for 1:9 SDBS / $C_{12}E_{10}$ was different i.e. at 9:1 and 5:5. SDBS / $C_{12}E_{10}$ k_1 value was = -45 kJ mol^{-1}

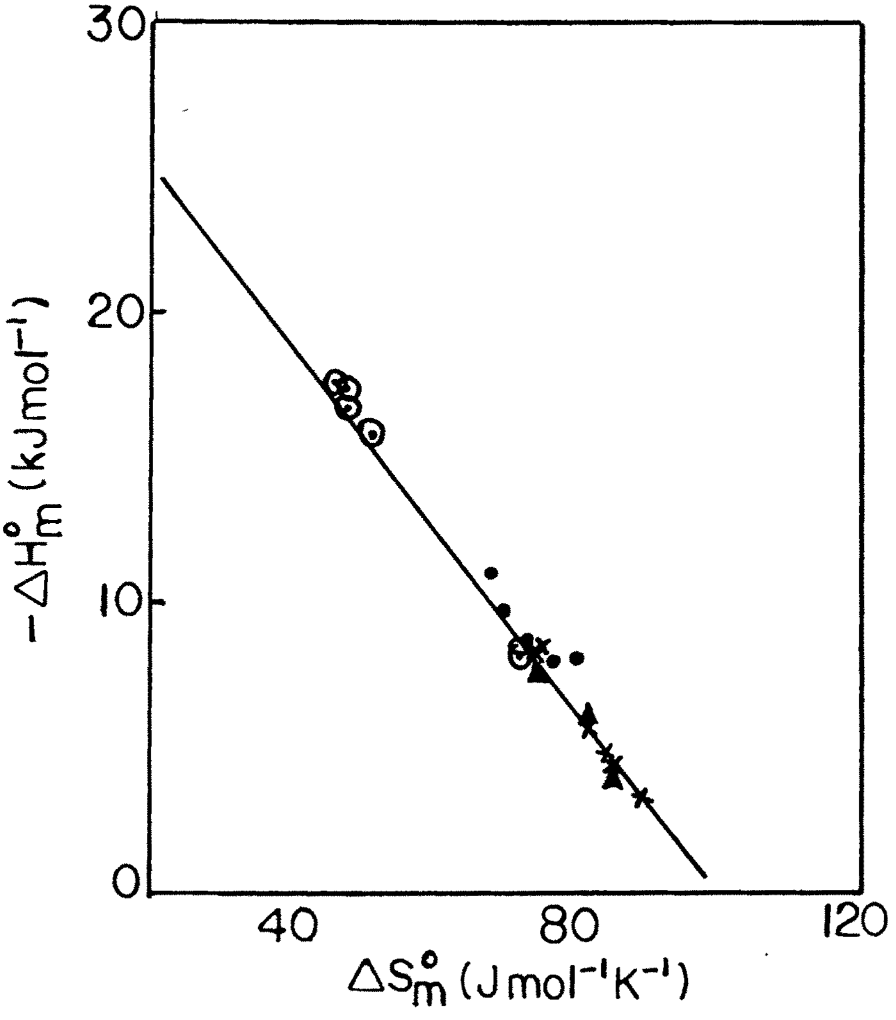

Fig. 13 : Enthalpy - Entropy compensation plot for Myrj 45 with all systems put together. ● PEG 400; ⊙ Sucrose; ✖ Acetamide; ▲ Urea.

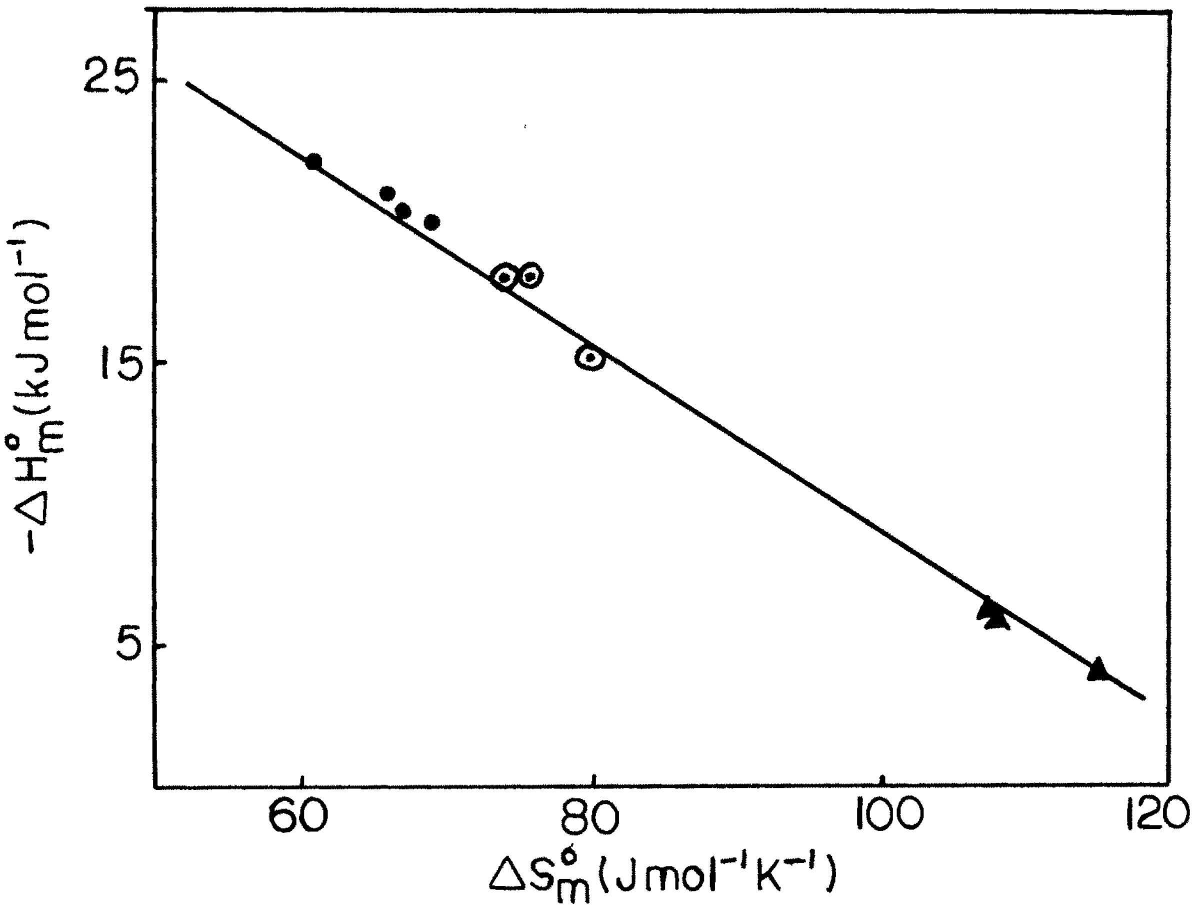

Fig. 14 : Enthalpy - Entropy compensation plot for $C_{12}E_{10}$ with all systems put together.

● PEG 400; ⊙ Sucrose; ▲ Urea.

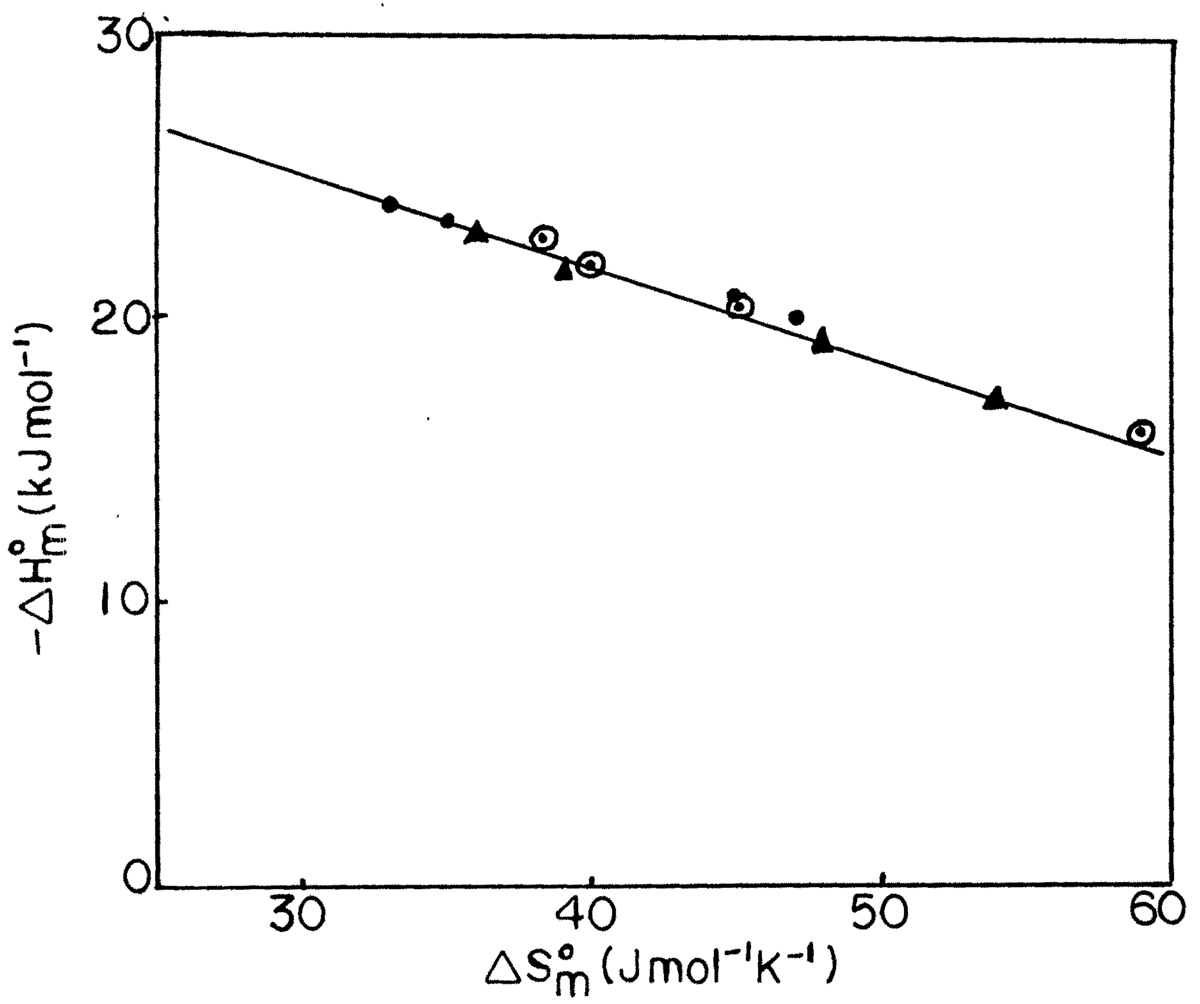

Fig. 15 : Enthalpy - Entropy compensation plot for SDBS with all systems put together.

● PEG 400; ⊙ Sucrose; ▲ Urea.

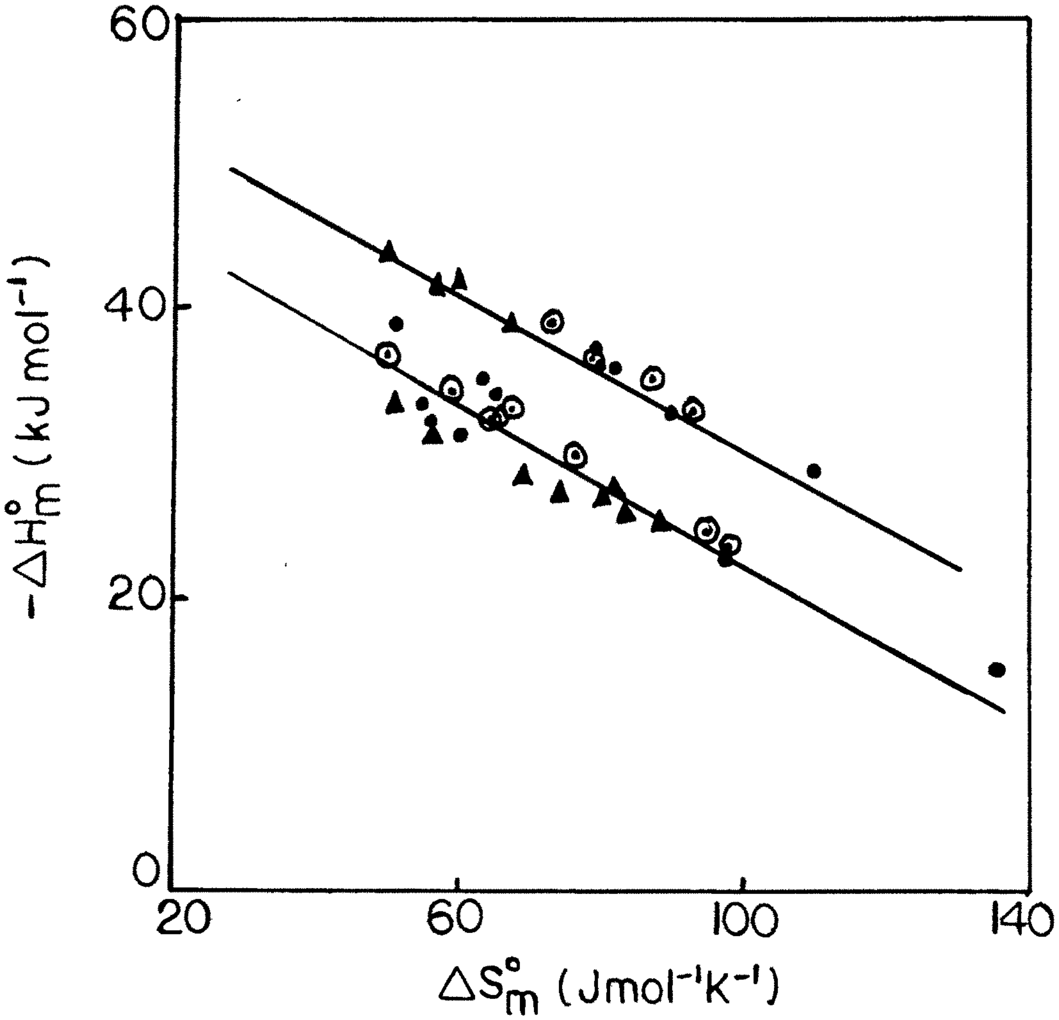

Fig. 16 : Enthalpy - Entropy compensation plot for SDBS / $C_{12}E_{10}$ mixed system in presence of additives. ● PEG 400; ⊙ Sucrose; ▲ Urea.

and at 1:9 ratio k_1 = -52 kJ mol^{-1}. As mentioned above higher the intercept, k_1, lower is the stability of micelle structure. Therefore, it can be assumed that at 1:9 SDBS / $C_{12}E_{10}$ the structure of micelles are relatively more stable than that at 5:5 and 9:1 ratios. This is also evident from the minimum observed in ΔG°_m Vs N_{SDBS} plot at $N_{SDBS} = 0.1$ indicating mixed micelle stability. However, it should be clear though that the linearity in ΔH°_m - ΔS°_m plots should not be over interpreted though this linearity is quite often seen[309].

The transfer enthalpy of micellization ($\Delta\Delta H^\circ{}_m{}^{tr}$) which is sensitive to the solvent structure has been computed from the following relation[55] -

$$\Delta\Delta H^\circ{}_m{}^{tr} = \Delta H^\circ_m \text{ (aq. Additive)} - \Delta H^\circ_m \text{ (water)}$$

The $\Delta\Delta H^\circ{}_m{}^{tr}$ for all our systems studied were found to be negative. Such negative transfer enthalpies have been reported earlier[97] for the transfer of amino acids and NaCl from water to aqueous urea solution. It was concluded that the transfer of hydrophilic groups from water to aqueous solutions is exothermic whereas that of hydrophobic groups is endothermic, the strong hydrophilic group - additive interaction being the dominating cause. The structure changing properties of both the hydrophobic (water structure making) and hydrophilic (water structure breaking) groups decrease in a less structured medium. This results in their opposing contributions to the $\Delta\Delta H^\circ{}_m{}^{tr}$ quantities. The decrease in the structure around the monomers in the solutions reflecting a greater structure breaking ability of these groups, may also be a reason for negative $\Delta\Delta H^\circ{}_m{}^{tr}$ values.

The rate of change of ΔH°_m with temperature is the specific heat of micellization, $\Delta C_{p\cdot m}$ with in Myrj 45. However, the variation of $\Delta C_{p,m}$ with concentration of the additives in all cases did not show any regularity. This was observed earlier in calorimetric studies[177].

The transfer heat capacities $\Delta\Delta C^{tr}_{p,m}$ were obtained using following relations[89].

$$\Delta\Delta C^{tr}_{p,m} = \Delta C_{p,m}\ (\text{aq. Additive}) - \Delta C_{p,m}\ (\text{water})$$

The transfer heat capacities of micellization $\Delta\Delta C^{tr}_{p,m}$ for the transfer of micelles from water to additive containing solutions are positive for most of the Myrj 45 systems (in presence of additives) indicating of increased hydration of micelles in these solutions due to greater extent of hydrogen bonding between ethylene oxide groups and additives present in solution. The $\Delta\Delta C^{tr}_{p,m}$ was positive for $C_{12}E_{10}$ system in presence of PEG 400 except at 1%, whereas in presence of sucrose the values were all negative. Negative $\Delta\Delta C^{tr}_{p,m}$ values can be attributed to a less structured medium compared to pure water. However, $\Delta\Delta C^{tr}_{p,m}$ shows a maximum for all systems as a function of additive concentration and this was observed earlier also by other workers. This maximum has been ascribed to micellar structural transitions[89, 105].

c) Adsorption Parameters :

It is well known that the air / solution interface of a surfactant solution is well populated by the adsorbed molecule. Accordingly, it has been shown that the concentration of the surfactant is always higher at the surface due to adsorption over and above the concentration of surfactant in the bulk.

The Gibb's equation[192] (in dilute systems) -

$$\Gamma = -\frac{1}{n\,RT}\,\frac{d\gamma}{d\ln C}\ \text{mol cm}^{-2}$$

where n = 1 and 2 for nonionic and ionic surfactants respectively and Γ, γ, R, T and C are the surface excess, concentration surface tension, gas constant, absolute temperature and total molar concentration of the surfactant respectively, can be used to determine the surface excess. The γ-log C plots for most of the systems were linear. However, for those systems wherein nonlinear plots were obtained, the curves were fitted to second order polynomial equation around a certain point. The coefficients of the polynomial equation $\gamma = a (\log C)^2 + b \log C + h$ were computed and hence

$$\mathbf{d\gamma / d \log C = 2 a \log C + b}$$

was calculated.

For $C_{12}E_{10}$ - additive systems i.e. PEG 400 and sucrose such nonlinear curves in γ-log C plots were observed (Fig. 17) and the surface excess, Γ, was calculated at $\log C = -5.4$ using the above polynomial equation. The corresponding uncertainity in **$d\gamma$ / d log C** was computed using the relation

$$\{(2 \Delta a \log C)^2 + (\Delta b)^2\}^{1/2}$$

Δa and Δb are the error in the coefficients a and b of the polynomial equation.

Similarly, the uncertainity in the surface tension value, γ, were calculated using the following relation at certain value of log C.

$$\text{i.e. } \{[\Delta a (\log C)^2]^2 + (\Delta b \log C)^2 + (\Delta h)^2]^{1/2}$$

Therefore, for $C_{12}E_{10}$ PEG 400 and sucrose systems the maximum error in $d\gamma$ / dlog C around $\log C = -5.4$ was found to be ~ 4% whereas the maximum error in γ (between calculated and experimental) around that point was found to be ~ 7%.

The surface excess values thus obtained for $C_{12}E_{10}$ - PEG 400, sucrose and urea systems are given in Tables 29-31. For pure $C_{12}E_{10}$ in absence of any additives the surface excess value increases with ~~rise in~~ increasing temperature. This is because as temperature increases the hydration of the ethoxy segment of nonionic surfactant decreases and hence greater tendency to locate at the air / water interface. However, in presence of PEG 400, sucrose and urea a reverse trend with respect to temperature was observed i.e. Γ decreases with ~~increase in~~ increasing temperature.

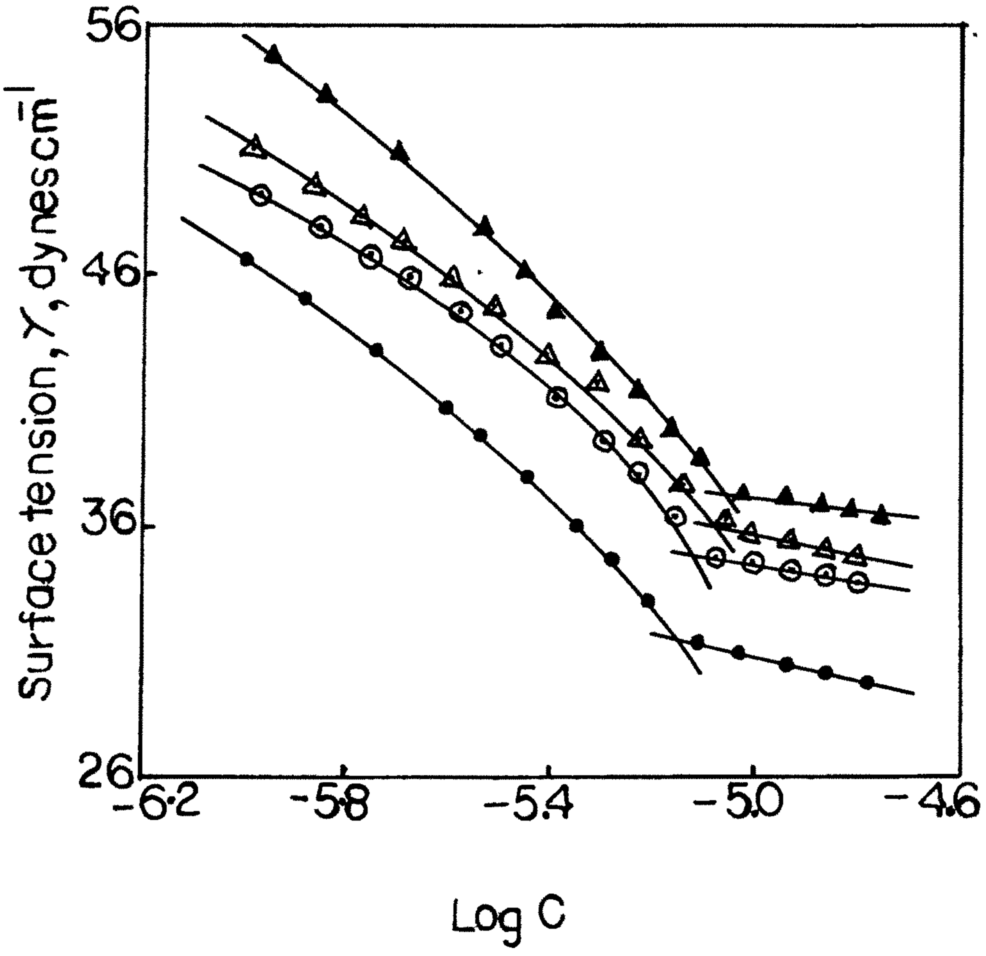

Fig. 17 : Surface tension (γ)-log C plot for $C_{12}E_{10}$ additive systems △ 0.3% PEG 400 at 50°C; ⊙ 0.3% PEG 400 at 45°C; ▲ Water at 45°C; ● 0.3% Sucrose at 40°C.

Table 29 : Surface excess (Γ X 10^{10} mol cm^{-2}) and area per molecule (A) for polyoxyethylene (10) lauryl ether ($C_{12}E_{10}$) in aqueous PEG 400 solution at different temperatures :

Conc. of PEG 400 % (w/v)	**Γ X 10^{10} mol cm^{-2}**				**A X 10^2 nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	2.3	2.4	3.3	3.6	72.2	69.2	50.3	46.1
0.05	5.2	5.2	3.7	2.7	31.9	31.9	44.9	61.5
0.1	4.8	4.6	3.1	2.4	34.6	36.1	53.5	50.3
0.3	4.8	3.5	2.7	2.4	34.6	47.4	61.5	69.2
0.5	3.4	3.4	2.3	3.4	48.8	48.8	72.2	48.8
0.7	2.6	2.3	2.3	1.2	63.8	72.2	72.2	138
1.0	2.1	3.1	2.8	2.6	79.1	53.5	59.3	63.8

Table 30 : Surface excess (Γ X 10^{10} mol cm^{-2}) and area per molecule (A x 10^{2} nm^{2}) for polyoxyethylene (10) lauryl ether in aqueous sucrose solution at different temperatures :

Conc. of Sucrose % (w/v)	**Γ X 10^{10} mol cm^{-2}**				**A X 10^{2} nm^{2}**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	2.3	2.4	3.3	2.6	72.2	69.2	50.3	46.1
0.05	2.8	2.5	2.4	1.7	--	--	--	--
0.1	3.0	2.2	2.1	2.0	50.3	75.5	79.1	83.0
0.3	3.5	3.1	2.0	1.6	47.4	53.5	83.0	103.8
0.5	3.0	2.7	1.9	1.5	50.3	61.5	87.4	110.7
0.7	2.5	2.1	2.4	2.1	66.4	79.1	69.2	79.1
1.0	2.7	2.6	1.7	1.5	61.5	63.8	63.8	110.7

Table 31 : Surface excess (Γ_{max} X 10^{10} mol cm^{-2}) and area per molecule (A_{min} x 10^2 nm^2) for polyoxyethylene (10) lauryl ether ($C_{12}E_{10}$) in aqueous urea solution at different temperatures :

Conc. of Urea % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^2 nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	2.3	2.4	3.3	3.6	72.2	69.2	50.3	46.1
0.1	3.2	2.8	2.7	2.6	51.5	58.5	61.3	64.2
0.3	3.1	2.9	2.8	2.6	52.9	56.8	59.5	64.2
0.5	3.2	3.2	2.8	2.6	51.6	51.5	59.5	64.2
0.7	3.4	3.1	2.9	2.7	48.9	53.4	56.2	60.4

In case of SDBS, an ionic surfactant, the Γ_{max} values was found to decrease in absence of any additive and increased when PEG 400, sucrose or urea was present. The Γ_{max} values are sown in Tables 32-34.

For SDBS / $C_{12}E_{10}$ mixed surfactant system(Table 35) the Γ_{max} values for the different mixtures i.e. mole ratios was found to lie in between those of pure components (Fig. 18). As the SDBS mole fraction increased in the mixture Γ_{max} decreased. Also, the Γ_{max} decreased as the temperature increases for SDBS / $C_{12}E_{10}$ mixtures a behavior similar to ionic surfactant as temperature rises leading to thermal agitation at the air / water interface.

The Γ_{max} values determined for SDBS / $C_{12}E_{10}$ in presence of PEG 400, sucrose and urea are given in Tables 36-44. The breaking of the solvent structure and probably a decreased freedom of motion of hydrocarbon chain are also reasons for such behavior. As the concentration of the additives are increased the Γ_{max} values are found to decrease at all the SDBS / $C_{12}E_{10}$ mole ratios studied (i.e. 1:9, 5:5 and 9:1). The most pronounced effects upon Γ_{max} comes from the nature of the polar head group. Such effect on Γ_{max} can be attributed to changed structure of the hydrophilic group of surfactant molecules caused by a probable interaction with the additive.

The minimum area per molecule (A_{min}) at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule, when the dimensions of the molecule with those obtained using molecular models. From the surface excess quantity, the limiting surface area per molecule of the surfactant (A_{min}), at the interface can be computed from the relation[193].

$$A_{min} = \frac{10^{14}}{N\,\Gamma_{max}} \quad nm^2$$

where N is the Avogadro number and Γ_{max} is surface excess in mol cm^{-2}.

Table 32 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS in aqueous sucrose solution at different temperatures :

Conc. of Sucrose % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.12	0.95	0.92	0.90	1.48	1.75	1.80	1.83
0.1	1.54	1.58	1.60	1.64	1.08	1.05	1.04	1.01
0.3	1.50	1.52	1.57	1.60	1.10	1.09	1.06	1.04
0.5	1.49	1.51	1.55	1.58	1.11	1.10	1.07	1.05
0.7	1.48	1.49	1.51	1.54	1.12	1.11	1.10	1.08

Table 33 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS in aqueous PEG 400 solution at different temperatures :

Conc. of PEG 400 % (w/v)	Γ_{max} X 10^{10} mol cm^{-2}				A_{min}, nm^2			
	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C
0.0	1.12	0.95	0.92	0.90	1.48	1.75	1.80	1.83
0.1	1.16	1.17	1.19	1.22	1.43	1.42	1.39	1.36
0.3	1.11	1.14	1.15	1.20	1.49	1.45	1.44	1.38
0.5	1.08	1.09	1.12	1.16	1.54	1.52	1.48	1.43
0.7	1.07	1.06	1.04	1.08	1.55	1.57	1.59	1.54

Table 34 : The maximum surface excess (Γ_{max}) minimum area per molecule (A_{min}) for SDBS in aqueous urea solution at different temperatures :

Conc. of Urea % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.12	0.95	0.92	0.90	1.48	1.75	1.80	1.83
0.1	1.18	1.20	1.23	1.28	1.41	1.38	1.35	1.30
0.3	1.17	1.19	1.21	1.25	1.42	1.39	1.37	1.33
0.5	1.14	1.15	1.17	1.23	1.45	1.44	1.42	1.35
0.7	1.12	1.14	1.20	1.21	1.48	1.46	1.38	1.37

Table 35 : The maximum surface excess (Γ_{max}) minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ mixed surfactant system at different temperatures and mole ratios :

SDBS / $C_{12}E_{10}$	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
10:1	1.12	0.95	0.92	0.90	1.48	1.75	1.80	1.83
9:1	1.18	1.14	1.13	1.12	1.39	1.45	1.47	1.48
7:3	1.19	1.16	1.14	1.13	1.38	1.43	1.45	1.47
5:5	1.21	1.17	1.15	1.13	1.37	1.42	1.44	1.46
3:7	1.41	1.52	1.21	1.14	1.18	1.26	1.37	1.46
1:9	1.58	1.47	1.34	1.27	1.05	1.13	1.24	1.31
0:10	2.31	2.36	3.27	3.60	0.72	0.70	0.51	0.46

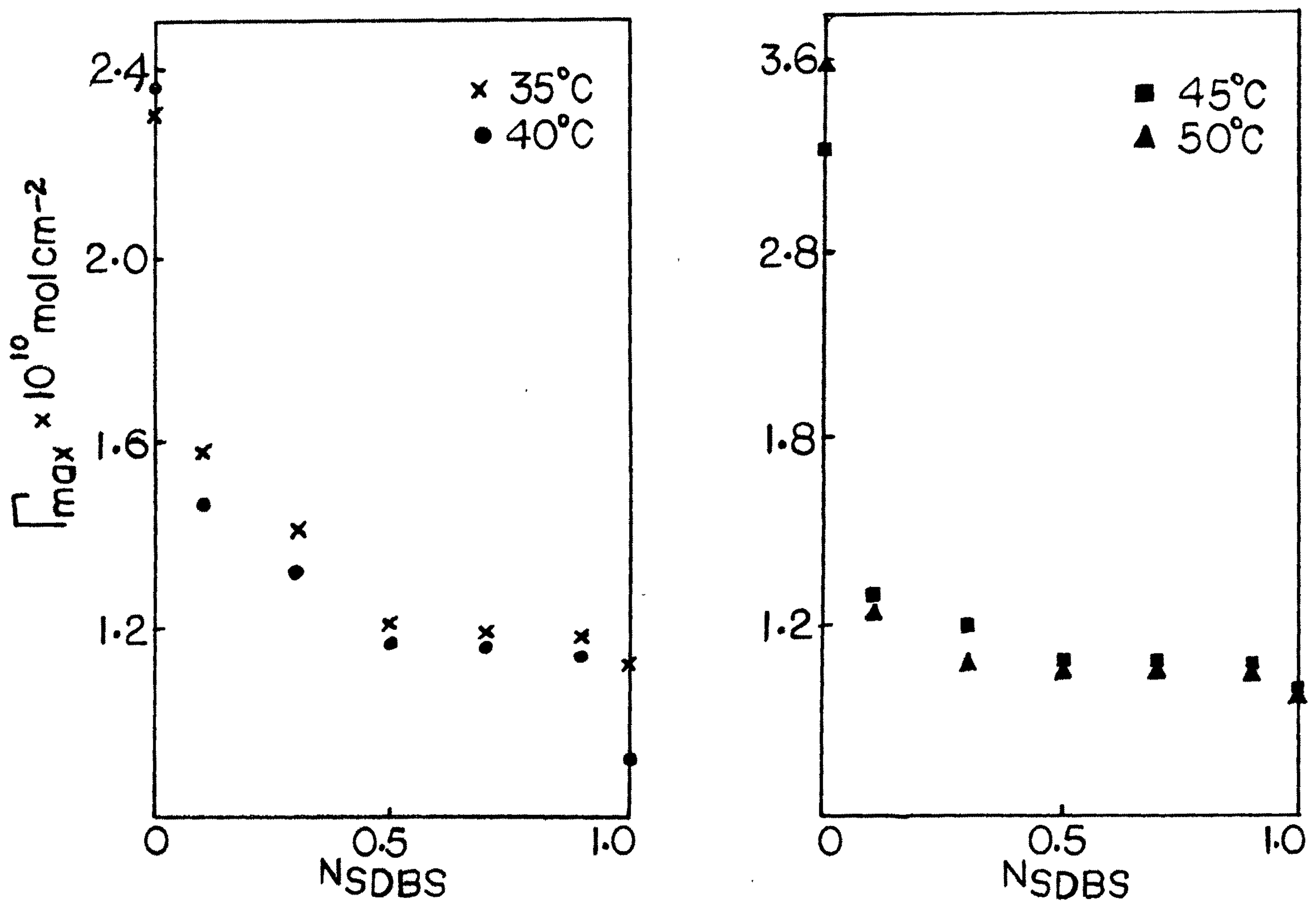

Fig. 18 : Maximum surface excess (Γ_{max}) at the air / water interface for SDBS / $C_{12}E_{10}$ at various SDBS mole fractions at different temperature.

Table 36 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous PEG 400 solution at different temperatures :

Conc. of PEG 400 % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.58	1.47	1.34	1.27	1.05	1.13	1.24	1.31
0.1	1.18	1.21	1.29	1.33	1.41	1.37	1.29	1.25
0.3	1.07	1.18	1.23	1.29	1.55	1.41	1.35	1.29
0.5	1.02	1.12	1.27	1.31	1.63	1.48	1.31	1.27
0.7	0.98	1.08	1.19	1.28	1.68	1.54	1.39	1.30

Table 37 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous sucrose solution at different temperatures :

Conc. of Sucrose % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.58	1.47	1.34	1.27	1.05	1.13	1.24	1.31
0.1	1.69	1.74	1.81	1.89	0.98	0.95	0.92	0.88
0.3	1.61	1.65	1.72	1.78	1.03	1.00	0.96	0.93
0.5	1.54	1.57	1.65	1.71	1.08	1.06	1.00	0.97
0.7	1.44	1.49	1.54	1.62	1.15	1.11	1.08	1.03

Table 38 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (1:9) mixed system in aqueous urea solution at different temperatures :

Conc. of PEG 400 % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.58	1.97	1.34	1.27	1.05	1.13	1.24	1.31
0.1	1.14	1.19	1.24	1.38	1.46	1.39	1.34	1.20
0.3	1.09	1.12	1.23	1.34	1.52	1.48	1.35	1.24
0.5	1.03	1.10	1.21	1.29	1.61	1.51	1.37	1.29
0.7	0.98	1.09	1.18	1.26	1.69	1.52	1.41	1.32

Table 39 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous PEG 400 solution at different temperatures :

Conc. of PEG 400 % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.21	1.17	1.15	1.13	1.37	1.42	1.44	1.46
0.1	1.02	1.17	1.26	1.32	1.63	1.42	1.32	1.26
0.3	1.02	1.10	1.17	1.21	1.63	1.51	1.42	1.37
0.5	0.97	1.02	1.07	1.20	1.70	1.63	1.43	1.38
0.7	0.98	1.00	1.05	1.16	1.68	1.66	1.58	1.43

Table 40 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous sucrose solution at different temperatures :

Conc. of Sucrose % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.21	1.17	1.15	1.13	1.37	1.42	1.44	1.46
0.1	1.61	1.68	1.71	1.77	1.03	0.99	0.97	0.94
0.3	1.49	1.57	1.64	1.69	1.11	1.06	1.01	0.98
0.5	1.42	1.53	1.59	1.59	1.17	1.08	1.04	1.00
0.7	1.42	1.50	1.61	1.61	1.17	1.10	1.03	0.96

Table 41 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (5:5) mixed system in aqueous urea solution at different temperatures :

Conc. of Urea % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.21	1.17	1.15	1.13	1.37	1.42	1.44	1.46
0.1	1.13	1.19	1.28	1.33	1.47	1.39	1.30	1.25
0.3	1.07	1.12	1.17	1.34	1.55	1.48	1.42	1.24
0.5	1.02	1.08	1.15	1.29	1.63	1.54	1.44	1.29
0.7	0.97	1.07	1.12	1.26	1.71	1.55	1.48	1.32

Table 42 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (9:1) mixed system in aqueous PEG 400 solution at different temperatures :

Conc. of PEG 400 % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.18	1.14	1.13	1.12	1.39	1.45	1.47	1.48
0.1	1.02	1.15	1.26	1.34	1.63	1.44	1.32	1.24
0.3	0.98	1.06	1.17	1.28	1.68	1.57	1.42	1.30
0.5	1.02	1.08	1.15	1.21	1.63	1.54	1.44	1.37
0.7	0.97	1.04	1.12	1.18	1.70	1.59	1.48	1.41

* Table 43 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS/ $C_{12}E_{10}$ (9:1) mixed system in aqueous sucrose solution at different temperatures :

Conc. of Sucrose % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.18	1.14	1.13	1.12	1.39	1.45	1.47	1.48
0.1	1.69	1.78	1.81	1.89	0.98	0.96	0.92	0.88
0.3	1.61	1.66	1.72	1.78	1.03	1.00	0.96	0.93
0.5	1.54	1.62	1.70	1.76	1.08	1.02	0.97	0.94
0.7	1.48	1.52	1.57	1.64	1.12	1.09	1.06	1.01

Table 44 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) of SDBS / $C_{12}E_{10}$ (9:1) mixed system in aqueous urea solution at different temperatures :

Conc. of Urea % (w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min}, nm^2**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	1.18	1.14	1.13	1.12	1.39	1.45	1.47	1.48
0.1	1.09	1.25	1.29	1.31	1.52	1.33	1.29	1.27
0.3	1.02	1.13	1.23	1.29	1.63	1.47	1.35	1.29
0.5	0.97	1.08	1.19	1.27	1.71	1.54	1.39	1.31
0.7	0.98	1.02	1.17	1.24	1.69	1.63	1.42	1.34

The minimum area per molecule occupied by the nonionic surfactant $C_{12}E_{10}$ as given in Table 29, decreases as temperature increases indicating a good packing at the air / water interface. However, once the additives are present the A_{min} values increases suggesting a poorer packing at the interface. Moreover, it is to be noted that the magnitudes of A_{min} are of the order of 1.42 nm^2 or less, indicating that the surface is a closed packed one and that the orientation of the surfactant molecules is almost perpendicular to the surface.

In case of pure SDBS in absence of additives A_{min} increases with temperature. The temperature dependence of A_{min} for even the SDBS / $C_{12}E_{10}$ combination showed an increase with respect to temperature, this is attributed to molecular motion at the air / water interface. In contrast to the effect observed in absence of additives for SDBS / $C_{12}E_{10}$ mixed system as temperature increased the A_{min} values decreased when additives are present (Tables 36-44). This can be ascribed to the fact that these additives lower the repulsion between the oriented ionic heads allowing a closer packing at the interface.

Hence, the overall observed effect can be attributed to various different factors such as (i) the changed structure around the head group due to the surfactant hydrophilic group - additive interaction; (ii) the changed nature of water in presence of these additives; (iii) the presence of additives at the air / water interface.

d) Thermodynamics of Adsorption :

The standard thermodynamic parameters of adsorption for $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ in presence and absence of additives, PEG 400, sucrose and urea were evaluated. The standard free energy of adsorption ΔG°_{ad} was calculated by the relation[33].

$$\Delta G^\circ_{ad} = RT \ln CMC - N \Pi_{CMC} A_{CMC}$$

where Π_{CMC} and A_{CMC} are the surface pressure and area per molecule at the CMC. The standard state here is a hypothetical monolayer at its minimum surface area per molecule but at zero surface pressure. The second term in the equation represents the surface work involved in going from zero surface pressure to Π_{CMC}, at constant minimum area per molecule, A_{min} ($=A_{CMC}$).

The effectiveness of a surface active molecule is measured by surface pressure 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 that of surfactant solution at CMC respectively. The Π_{CMC} is generally found to be higher at higher temperature for nonionic surfactant (this higher adsorption at the interface) indicates greater hydrophobicity of nonionics at higher temperature. In the SDBS / $C_{12}E_{10}$ mixed system as the mole fraction of $C_{12}E_{10}$ is increased, there are higher adsorption at the interface due to weak ion-ion repulsion.

As given in Tables 45-50 for SDBS and $C_{12}E_{10}$ both in presence and absence of additives ΔG°_{ad} values were all negative indicating a spontaneous adsorption process. The magnitudes of ΔG°_{ad} in presence of additive were always more negative compared to that in absence indicating that when a micelle is formed work has to be done to transfer the surfactant molecule in the monomeric form from the surface to the micellar stage through aqueous medium[61].

With increasing temperature, the ΔG°_{ad} values are less negative (in absence of additives) suggesting that relatively more energy is required for the adsorption to occur. In the presence of additives the values become more negative with respect to temperature increase, implying that the dehydration of the hydrophilic group is required for the adsorption to take place and that since at higher temperature, the surfactant is less hydrated, comparatively less energy is required for adsorption.

In Table 51 the ΔG°_{ad} values for SDBS / $C_{12}E_{10}$ mixed system are shown. It is observed that ΔG°_{ad} values were more negative for the mixtures at all mole ratios

Table 45 : Thermodynamic parameters of adsorption of polyoxyethylene (10) lauryl ether in presence of aqueous PEG 400 solution :

Conc. of PEG 400 % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	52.1	54.5	51.2	47.3	-257	-0.67
0.05	44.7	48.5	47.4	54.3	151	0.64
0.1	45.1	44.5	47.6	48.2	22	0.22
0.3	44.6	47.5	54.9	49.8	57	0.33
0.5	45.7	45.1	45.7	46.2	-11	0.11
0.7	48.9	51.0	48.7	59.3	172	0.72
1.0	48.9	48.0	49.2	51.2	49	0.32

Table 46 : Thermodynamic parameters of adsorption of polyoxyethylene (10) lauryl ether in presence of aqueous sucrose solution :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	52.1	54.5	51.2	47.3	-257	-0.67
0.05	49.7	50.6	50.6	51.3	-18.1	0.102
0.1	45.6	51.3	55.3	62.7	295	1.10
0.3	46.8	44.5	57.8	64.6	315	1.18
0.5	48.0	49.9	53.9	66.0	447	1.61
0.7	47.7	50.3	50.4	52.8	54	0.33
1.0	48.6	48.1	53.6	56.4	109	0.51

Table 47 : Thermodynamic parameters of adsorption of polyoxyethylene (10) lauryl ether in presence of aqueous urea solution :

Conc. of Urea % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (kJ mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	52.1	54.5	51.2	47.3	-257	-0.67
0.1	46.4	47.7	48.7	49.4	14.5	0.198
0.3	46.4	47.1	48.2	49.3	14.1	0.196
0.5	46.2	47.1	48.5	49.5	22.6	0.223
0.7	46.2	47.4	48.0	48.8	6.9	0.173

Table 48 : Thermodynamic parameters of adsorption of sodium dodecyl benzene sulfonate (SDBS) in presence of aqueous PEG 400 solution :

Conc. of PEG 400 % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	59.7	61.7	62.0	63.1	-3.2	205
0.1	50.5	50.9	51.4	51.9	21.5	94
0.3	51.8	52.3	52.7	53.2	23.7	91
0.5	53.7	54.3	54.7	55.1	24.3	96
0.7	54.1	54.5	55.0	55.0	24.7	95

Table 49 : Thermodynamic parameters of adsorption of sodium dodecyl benzene sulfonate (SDBS) in presence of aqueous sucrose solution :

Conc. of Sucrose % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	59.7	61.7	62.0	63.1	-3.2	205
0.1	52.0	52.4	52.9	53.5	22.3	96
0.3	53.8	54.1	54.4	5438	33.2	66
0.5	52.7	53.2	53.7	54.3	19.8	106
0.7	53.1	53.5	53.8	54.1	32.8	66

Table 50 : Thermodynamic parameters of adsorption of sodium dodecyl benzene sulfonate (SDBS) in presence of aqueous urea solution :

Conc. of Urea % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	59.7	61.7	62.0	63.1	-3.2	205
0.1	52.3	52.7	53.2	53.6	26.2	85
0.3	52.7	53.1	53.7	54.0	24.2	92
0.5	52.5	53.0	53.4	53.9	24.8	90
0.7	53.7	54.0	54.5	54.9	28.3	82

Table 51 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ mixed system at different mole ratios :

SDBS / $C_{12}E_{10}$	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
10:0	59.7	61.7	62.0	63.1	3.2	205
9:1	76.2	78.0	79.3	80.7	14.7	296
7:3	77.7	79.6	81.2	82.7	23.5	329
5:5	79.9	81.8	83.5	84.8	20.9	328
3:7	79.9	82.0	84.5	86.8	63.5	465
1:9	80.4	82.5	85.0	86.8	53.5	434
0:10	52.1	54.5	51.2	47.8	-257	-670

compared to pure components. This suggests that adsorption of mixtures is relatively more spontaneous especially at $N_{SDBS} = 0.1$ (Fig.19). However, as observed from Tables 52-60 in presence of additives for SDBS / $C_{12}E_{10}$ system the ΔG°_{ad} values are more negative, indicative of relatively less spontaneous adsorption of the mixtures.

The standard enthalpy of adsorption (ΔH°_{ad}) and entropy of adsorption (ΔS°_{ad}) were computed using the well known relation -

$$\frac{\delta (\Delta G^{\circ}_{ad})}{\delta T} = - \Delta S^{\circ}_{ad}$$

$$\Delta G^{\circ}_{ad} = \Delta H^{\circ}_{ad} - T \Delta S^{\circ}_{ad}$$

As observed from the tabulated data for $C_{12}E_{10}$ and SDBS in absence of any additive the process of adsorption was found to be exothermic and endothermic respectively. Similar endothermic contribution to the adsorption process was observed for SDBS / $C_{12}E_{10}$ mixed system. But, in presence of PEG 400, sucrose and urea for SDBS / $C_{12}E_{10}$ mixed system showed an endothermic contribution. Such exothermic / endothermic contribution towards adsorption process can be ascribed to whether bond making or bond breaking predominates during adsorption[86]. The overall exothermicity observed can also be accounted for by the surfactant hydrophilic group - additive interaction.

The standard entropy of adsorption ΔS°_{ad}, was negative for $C_{12}E_{10}$ in absence of any additive suggesting a well ordered structure at the air / water interface. In presence of PEG 400, sucrose and urea a positive ΔS°_{ad} values were obtained which may be ascribed to a larger freedom of motion of the hydrocarbon chains at the interface and also due to mixing of surfactants with additive molecules. Similarly, for SDBS / $C_{12}E_{10}$ mixed system a positive ΔS°_{m} was observed in presence and absence of additives. It should be mentioned here that in presence of additives the lowering of

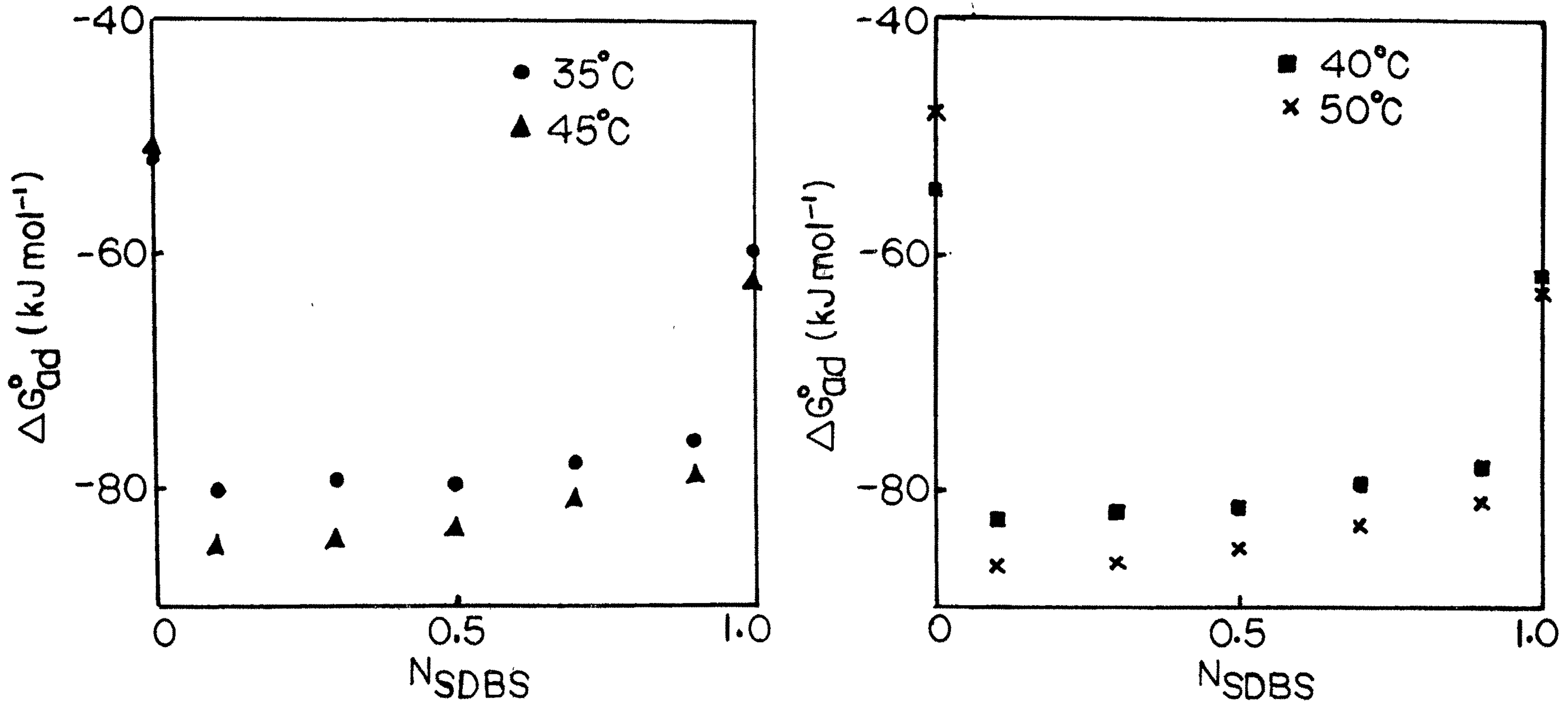

Fig. 19 : ΔG°_{ad} - mole fraction of SDBS for SDBS / $C_{12}E_{10}$ mixed system at different temperature.

Table 52 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (1:9) mixed system in presence of aqueous PEG 400 at different mole ratios :

Conc. of PEG 400 % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	80.4	82.5	85.0	86.8	-53.5	434
0.1	83.7	84.6	85.4	85.4	34.9	158
0.3	85.6	86.2	86.9	87.6	44.3	134
0.5	84.6	85.4	86.1	86.8	41.1	141
0.7	85.6	86.4	87.1	87.7	41.9	142

Table 53 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (1:9) mixed system in presence of aqueous sucrose solution :

Conc. of Sucrose % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	80.4	82.5	85.0	86.8	-53.5	434
0.1	76.8	77.5	78.1	79.0	32.7	143
0.3	76.6	77.6	78.5	79.4	18.3	189
0.5	78.5	79.4	80.2	21.1	23.9	177
0.7	79.3	80.1	81.0	82.1	19.2	194

Table 54 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (1:9) mixed system in presence of aqueous urea solution :

Conc. of Urea % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	80.4	82.5	85.0	86.8	-53.5	434
0.1	85.3	86.2	86.8	87.5	40.1	147
0.3	84.3	85.1	85.8	86.5	39.1	147
0.5	83.6	84.3	85.1	85.8	37.9	148
0.7	83.1	83.9	84.6	85.3	38.2	146

Table 55 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (5:5) mixed system in presence of aqueous PEG 400 solution :

Conc. of PEG 400 % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	79.9	81.1	83.5	84.8	-20.9	328
0.1	74.5	75.3	76.1	76.9	24.9	161
0.3	77.6	78.3	79.1	79.9	29.3	157
0.5	76.2	76.9	77.5	78.2	36.4	129
0.7	78.0	78.7	79.5	80.3	30.4	154

Table 56 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (5:5) mixed system in presence of aqueous sucrose solution :

Conc. of Sucrose % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	79.9	81.8	83.5	84.8	-20.9	328
0.1	70.6	71.1	71.8	72.6	28.2	137
0.3	72.4	73.3	73.9	74.8	24.2	157
0.5	71.1	71.8	72.6	73.3	25.0	150
0.7	70.3	71.1	71.9	72.8	18.1	169

Table 57 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (5:5) mixed system in presence of aqueous urea solution :

Conc. of Urea % (w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	79.9	81.8	83.5	84.8	-20.9	328
0.1	79.1	79.7	80.3	80.9	41.3	123
0.3	78.2	78.8	79.4	79.9	42.6	115
0.5	77.5	78.2	78.8	79.4	38.2	127
0.7	77.3	77.9	78.6	79.3	34.9	138

Table 58 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (9:1) mixed system in presence of aqueous PEG 400 solution :

Conc. of PEG 400 % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	76.2	78.0	79.3	80.7	-14.7	296
0.1	75.3	76.0	76.6	77.1	38.1	121
0.3	75.5	76.2	76.8	77.4	36.6	126
0.5	75.1	75.7	76.5	77.3	30.3	145
0.7	76.4	77.2	77.9	78.7	30.8	148

Table 59 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (9:1) mixed system in presence of aqueous sucrose solution :

Conc. of Sucrose % (w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	35°C	**40°C**	**45°C**	**50°C**		
0.0	76.2	78.0	79.3	80.7	-14.7	296
0.1	64.2	65.2	66.0	66.5	16.7	155
0.3	65.7	66.5	67.4	68.4	11.2	177
0.5	65.8	66.7	67.6	68.3	13.1	171
0.7	66.3	67.1	68.1	68.1	10.6	180

Table 60 : Thermodynamic parameters of adsorption of SDBS / $C_{12}E_{10}$ (1:9) mixed system in presence of aqueous urea solution :

Conc. of Urea % (w/v)	$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})	ΔS°_{ad} (J mol^{-1} K^{-1})
	35°C	40°C	45°C	50°C		
0.0	76.2	78.0	79.3	80.7	-14.7	296
0.1	75.4	75.9	76.5	77.2	38.2	121
0.3	76.8	77.4	78.0	78.5	41.1	116
0.5	76.0	76.6	77.1	77.7	40.4	115
0.7	75.7	76.3	76.9	77.6	38.2	122

electrostatic repulsion between ionic species at the air / water interface reduces the freedom of motion of the hydrocarbon chains leading to lower ΔS^{o}_{ad} values.

e) Cloud Points :

Cloud points are the manifestation of the solvation / desolvation phenomena in nonionic surfactant solutions[311-312]. The desolvation of the hydrophilic groups of the surfactant leads to the formation of cloud in surfactant solution. In Fig. 20, we present the cloud points of Myrj 45 surfactants in presence of different concentration of PEG 400, sucrose, urea and acetamide. Similarly, Fig. 21 shows the cloud point of $C_{12}E_{10}$ in presence of additives. In both the cases in the presence of PEG 400 and sucrose the cloud point decreases. This indicates that additives remove water from near the micelle thereby help the micelles to approach each other easily. It was stated by Kjellander et al.[311] that the appearance of the cloud point is entropy dominated. The ethylene oxide group is highly hydrated, and the nonionic micelles are expected to have water deep inside the micelle. As these additives are added, the water of hydration of the micelles decrease because the additives compete for the water molecules with the micelles. Now with the two relatively less hydrated micelles approaching each other, the hydration spheres overlap and some water molecules are freed to increase the entropy of the system. At the cloud point, the water molecules get totally detached from the micelles. The overall entropy is very high and hence the free energy change is relatively more negative[118], and the appearance of the cloud point is facile.

However, water structure breakers such as acetamide and urea help in the solvation of the surfactant hydrophilic group. It was observed earlier also[98], that water structure breakers generally increase the cloud point of nonionic surfactants e.g. of T X 100. The increase in the cloud point of nonionic surfactant in presence of urea has been explained on the basis of direct mechanism of urea action, wherein, if urea replaces some water molecules in the hydration layer of the micelle, a thicker hydration layer is formed and as a result steric repulsions between the micelles increase. Moreover,

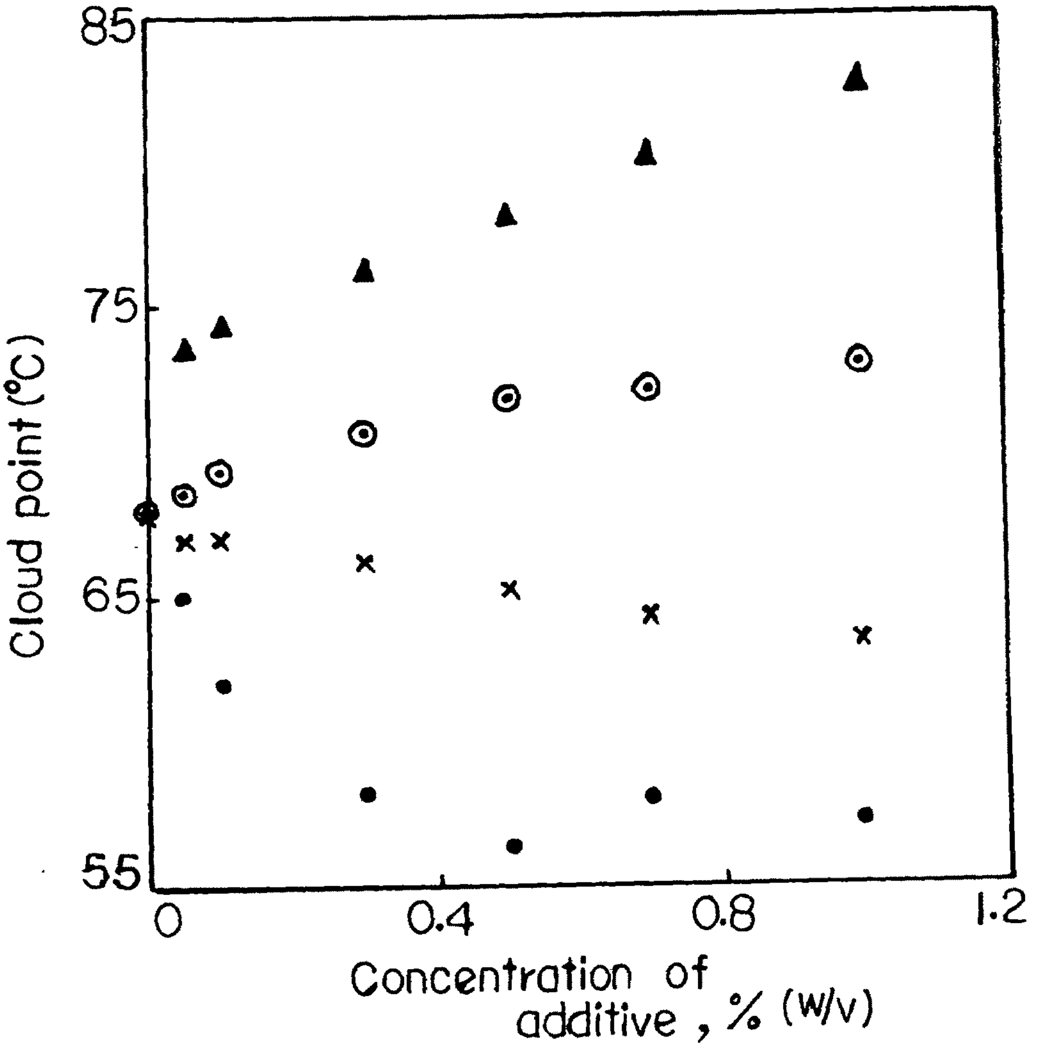

Fig. 20 : Effect of additives on the cloud point of Myrj 45 (0.1% w/v). ● PEG 400; ✖ Sucrose; ⊙ Acetamide; ▲ Urea.

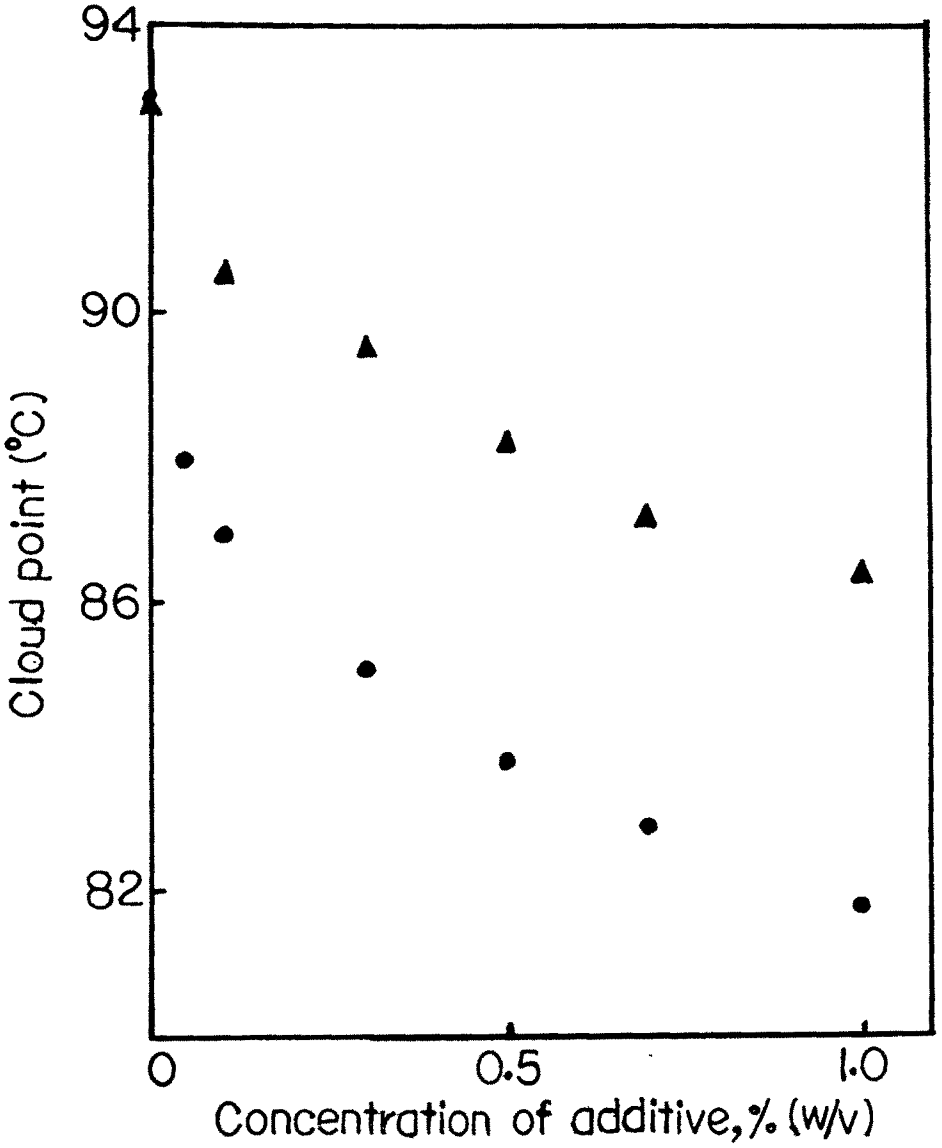

Fig. 21 : Effect of additives on the cloud point of $C_{12}E_{10}$ (1% w/v). ▲ Sucrose; ● PEG 400.

the water structure breakers increase the cloud point by making more water molecules available to interact with the polyoxyethylene chain of the nonionic surfactant, in other words, urea helps in the solvation of hydrophilic group of the surfactant.

In Fig. 22, the effect of SDBS on the cloud point of $C_{12}E_{10}$ is shown. The concentration of SDBS was kept constant and that of $C_{12}E_{10}$ was varied. The SDBS concentration studied were 2 and 5 x 10^{-4}M. At both these concentrations of SDBS an increase in the cloud point of $C_{12}E_{10}$ was observed. However, it is to be noted that at lower concentration of $C_{12}E_{10}$ the increase in the cloud point is higher. The cloud point increase here is due to the formation of mixed micelles, that are charged. Such behavior has been observed earlier by Marszall[312] and also by Valaulikar et al.[313]. The lower the $C_{12}E_{10}$ concentration in the mixture (i.e. more SDBS) higher will be the charge density of the mixed micelle, the repulsive forces become more prominent, hence higher the temperature for clouding.

At a particular $C_{12}E_{10}$ concentration, when SDBS concentration is increased then CP * increases again indicative of increase in micellar charge density. Hence, it is the charge density here that decides the cloud point. The higher the charge density, the higher the cloud point. As the charge density is dependent on the micelle size, the increase in the concentration of any kind of additive does not always increase the charge density of the micelle.

f) Micellar Aggregation Number (N_{agg}) :

The micellar aggregation number (N_{agg}) ~~is~~ may be determined by a number of methods such as * light scattering[314], NMR self diffusion coefficients[315], small angle neutron scattering (SANS)[316], freezing point[317] vapour pressure methods[318] and fluorescence probe[287] methods. The most common and widely used of all these methods is the fluorescence technique.

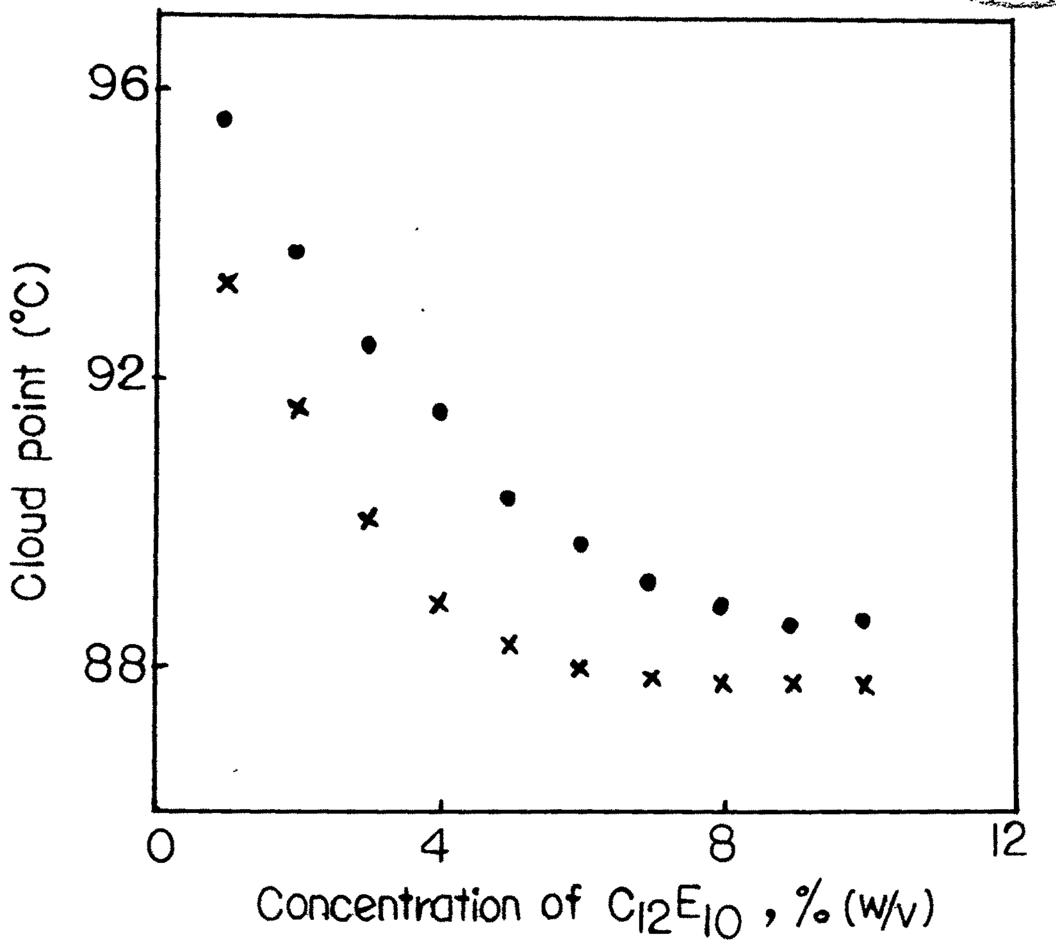

Fig. 22 : Effect of SDBS on the cloud point of $C_{12}E_{10}$ of different concentrations. ✖ 2 x 10^{-4}M SDBS; ● 5 x 10^{-4}M SDBS.

We have made use of the steady state fluorescence quenching method of Turro and Yekta[287]. The Fig. 23, show the plot of micellar aggregation of SDBS for SDBS / $C_{12}E_{10}$ mixed surfactant system. It indicates a synergistic effect in the aggregation number. The values obtained at various mole fractions of SDBS in the mixed system is always larger than either of the two pure components and such a behavior can be ascribed to two competing factors[319,320] (i) nonionic surfactants show a lower aggregation number due to increased steric forces. However, as the anionic SDBS incorporates into the micelle the steric interactions are decreased compared to pure $C_{12}E_{10}$ micelle; (ii) due to the presence of interionic interactions ionic surfactants have low aggregation number when the nonionic $C_{12}E_{10}$ gets incorporated into the micelle the interionic interactions are decreased compared to pure SDBS micelle. Consequently, the repulsive head group interactions are much reduced leading to larger mixed micelle compared to pure $C_{12}E_{10}$ or SDBS.

The micellar aggregation number (N_{agg}) was also determined for $C_{12}E_{10}$, SDBS and SDBS / $C_{12}E_{10}$ mixtures at different concentrations of PEG 400, sucrose and urea at room temperature. The data are shown in Table 61. In presence of these additives the N_{agg} values were considerably lowered. As mentioned earlier that both PEG 400 and sucrose due to their presence of -OH groups i.e. hydrogen bonding ability with solvent have major effect on the water at the micellar hydrocarbon-water interface. Also, it has been reported that urea replaces some water molecules in the solvation layer of the micelle head groups, leading to direct participation of urea in the solvation of the micelle. Since, the urea molecule is 2.5 times larger than a water molecule[88] and the substitution of water molecules by urea molecules will cause an increase in the surface area per head group, thereby, lowering the aggregation number. It is to be noted that the extent of decrease in N_{agg} values is same in presence of PEG 400, sucrose as well as urea. The overall effect is indicative of the hindrance in the micelle formation in presence of these additives and all the three additives seem to provide the same amount of hindrance. However, with definite increase in the concentration of the additives a small increase in the aggregation number was observed. It is to be

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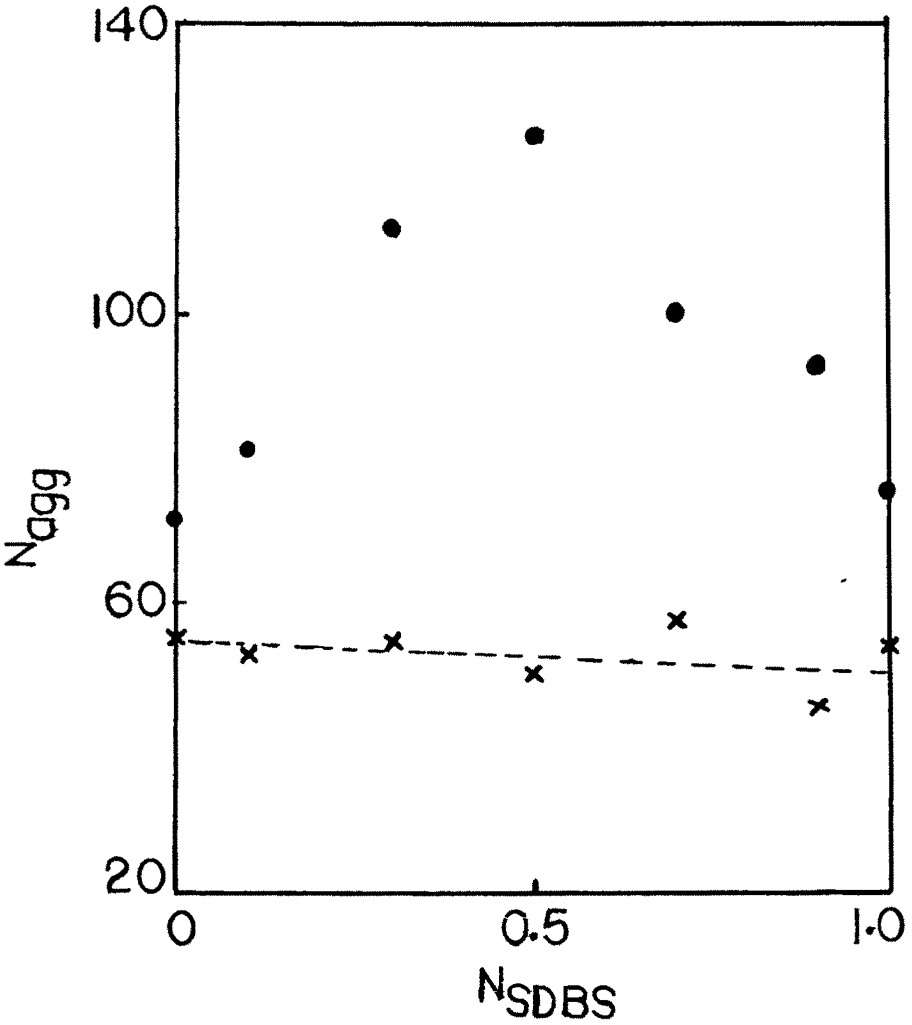

Fig. 23 : The aggregation number (N_{agg}) against SDBS mole fraction.

Table 61 : The micellar aggregation number (N_{agg})of pure and mixed SDBS / $C_{12}E_{10}$ mixed system in presence and absence of additives :

SDBS / $C_{12}E_{10}$	N_{agg}												
	No Additive	PEG 400				Sucrose				Urea			
		0.1	0.3	0.5	0.7% (w/v)	0.1	0.3	0.5	0.7% (w/v)	0.1	0.3	0.5	0.7% (w/v)
0.0	72	56	55	62	65	55	51	55	59	51	54	58	60
0.1	81	43	53	55	58	43	58	60	65	60	63	73	78
0.3	112	48	55	60	68	42	56	58	63	50	55	60	65
0.5	124	49	50	50	64	63	65	70	68	50	58	65	70
0.7	93	50	58	60	63	40	45	50	55	43	48	55	58
0.9	99	40	45	48	53	40	43	45	50	48	50	58	60
1.0	75	61	54	58	60	62	68	66	69	68	66	69	68

noted that although a maximum is observed at 0.5 mole fraction of SDBS in presence of these additives, almost all the mixed systems show the same aggregation number. The N_{agg} values were 51 ± 3, 55 ± 3, 59 ± 3 and 63 ± 3 for 0.1%, 0.3%, 0.5% and 0.7% (w/v) additive concentrations respectively at all SDBS / $C_{12}E_{10}$ mole ratios. The maximum error in N_{agg} was found to be ± 6%.

g) Interaction Parameter (β) :

The interaction between the surfactant molecules in the mixed micelle was computed using Rubingh's regular solution approach[130].

$$\beta^m = \ln [(CMC\ \nu / CMC_1\ X_1^M)] / (1 - X_1^M)^2$$

where β^m is the interaction parameter, ν is the mole fraction of ionic surfactant in solution, X_1^M is the ionic surfactant mole fraction in the mixed micelle, CMC and CMC_1 are the critical micelle concentrations of the mixture and that of ionic surfactant respectively. X_1^M is determined by solving the following equation iteratively.

$$\frac{(X_1^M)^2 \ln [\nu\ CMC / X_1^M\ CMC_1)]}{(1-X_1^M)^2 \ln [(1-\nu)\ CMC / (1-X_1^M)\ CMC_2]} = 1$$

where CMC_2 is the critical micelle concentration of the nonionic surfactant.

The β^m values computed for SDBS / $C_{12}E_{10}$ mixed system are shown in Table 62. It is observed that these values are negative throughout at all mole fractions of SDBS as well as at all temperatures. Such negative values for β^m have been reported earlier also for anionic / nonionic binary surfactant mixtures. This can be attributed to the attractive interaction between SDBS and $C_{12}E_{10}$ head groups leading to electrostatic stabilization. It has been suggested that nonionic surfactants of polyoxyethylene types

Table 62 : Interaction parameter (β^m) between the surfactant molecules in mixed micelle at different temperatures for SDBS / $C_{12}E_{10}$ mixed system :

SDBS / $C_{12}E_{10}$	**β^m**			
	35°C	**40°C**	**45°C**	**50°C**
9:1	-8.9	-8.3	-8.1	-7.9
7:3	-9.3	-8.0	-8.2	-8.0
5:5	-9.8	-8.8	-8.5	-8.4
3:7	-10.5	-9.4	-9.5	-9.3
1:9	-12.1	-11.0	-10.8	-11.5

have a weakly cationic character resulting from the oxonium ion formation with protons from water[321]. The resultant attractive interaction may probably be due to this oxonium ion with anionic surfactant. Further, it is interesting to note that β^m values are more negative as the mole fraction of SDBS decreases. Also, β^m is less negative at higher temperatures indicating greater repulsion between the ionic heads in the mixed micelle.

The interaction parameter β^σ between the surfactant molecules in the mixed monolayer was determined. From surface tension - log concentration plots for each of the two pure surfactants in the system and one for the mixture at fixed ν value are required. For calculating β^σ at the air / water interface C_1°, C_2° and C_{12}° are required in place of CMC_1, CMC_2 and CMC respectively in the above equation. X_1^M is replaced by X_1° which is the mole fraction of ionic surfactant in the mixed monolayer. C_1°, C_2° and C_{12}° are the solution phase molar concentrations of ionic and nonionic surfactants and their mixture, respectively required to produce a given surface tension value (Fig. 24).

i.e.

$$\frac{(X_1^\sigma)^2 \ln [(\nu C_{12}^0) / X_1^\sigma, C_1^\circ]}{(1 - X_1^\sigma)^2 \ln [(1-\nu) C_{12}^O / (1- X_1^\sigma) C_2^\circ]} = 1$$

and

$$\beta^\sigma = \ln [(C_{12}^O \nu / C_1^\circ X_1^\sigma)] / (1-X_1^\sigma)^2$$

The β^σ values thus calculated for SDBS - $C_{12}E_{10}$ mixed system are given in Table 63.

The β^σ values were found to be negative at all mole fractions of SDBS although the β^m values were always more negative than β^σ. This suggests that the attractive interaction is comparatively more in the mixed micelle than in the mixed monolayer.

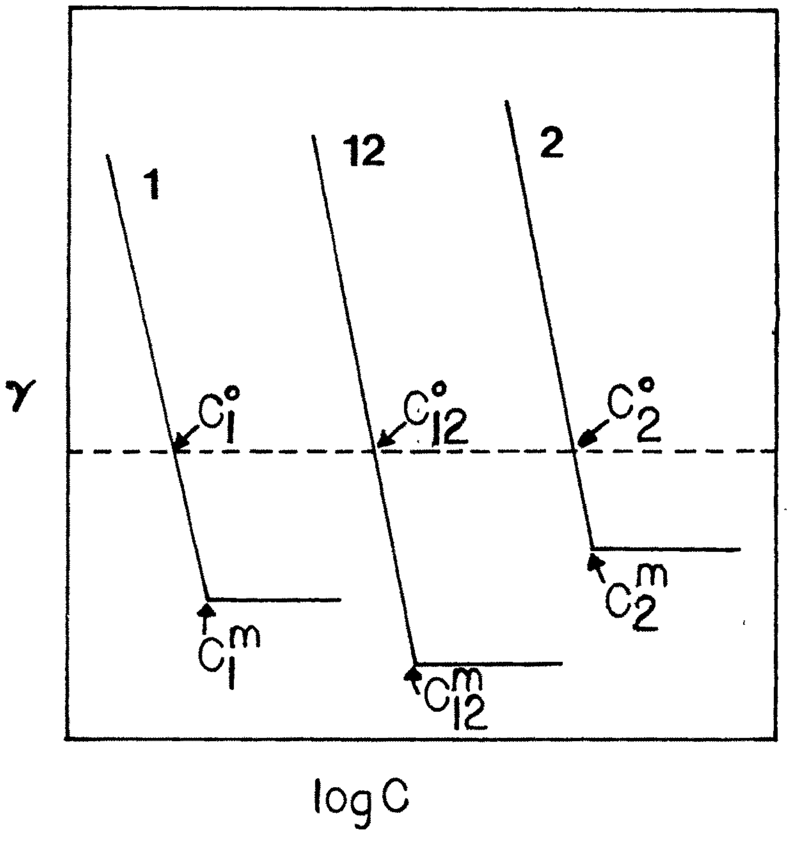

Fig. 24 : Experimental evaluation of β^o and β^m (1) pure surfactant 1 (2) pure surfactant 2 (12) mixtures of surfactants 1 and 2 at a fixed mole fraction ν in solution C_1^o, C_2^o and C_{12}^o are the concentrations of surfactant 1, 2 and 12 respectively at fixed value of surface tension (γ). (taken from ref. 29).

Table 63 : Interaction parameter (β^{σ}) between the surfactant molecules in mixed monolayer at air / water interface for SDBS / $C_{12}E_{10}$ mixed system at different temperatures :

SDBS / $C_{12}E_{10}$	**β^{σ}**			
	35°C	**40°C**	**45°C**	**50°C**
9:1	-4.2	-3.3	-2.6	-1.4
7:3	-6.2	-4.5	-3.7	-1.8
5:5	-8.2	-5.8	-4.7	-2.3
3:7	-8.3	-6.8	-5.8	-3.3
1:9	-10.6	-7.9	-6.1	-6.7

Similarly, the β^m values for SDBS / $C_{12}E_{10}$ mixed system at 0.1, 0.5 and 0.9 SDBS mole fraction in presence of PEG 400, sucrose and urea were deduced and the values are shown in Tables 64-66. Although, all the values were found to be negative, indicating an attractive interaction even in presence of additives, the magnitudes were not as large negative as in the absence of any additive. This itself shows that these additives show a marked effect in the interaction between the surfactant molecules in mixed micelle.

The additives PEG 400, sucrose and urea, as mentioned before are likely to be present at the micelle - solvent interface. Due to this, the attractive interaction between the SDBS and $C_{12}E_{10}$ surfactants is drastically reduced and the interaction parameter β^m becomes less negative.

h) Partition Coefficients :

The partition coefficients P of neutral solutes between the micelles and water can be deduced from the analysis of the variation of critical micelle concentration (CMC) of the surfactant on the addition of solute. The pseudo phase model has been adopted for the calculations of partition coefficients[93, 322].

Hence, adopting the pseudo phase model and assuming a thermodynamic equilibrium for the surfactant monomer between the bulk phase and the micellar phase and neglecting the activity coefficients contribution, the chemical potential in case of dilute solution of 1:1 ionic surfactant can be written as -

$$\mu_{s,w} = \mu^{o}_{s,w} + 2\,RT\ \ln CMC_W$$

where CMC_W is the CMC of surfactant in water and $\mu_{S,W}$ and $\mu_{S,W}{}^{o}$ are the standard chemical potentials of monomer in the bulk and the micelle phase respectively. The surfactant chemical potential in the pseudo micellar phase may be written as -

Table 64 : Interaction parameter (β^m) for SDBS / $C_{12}E_{10}$ mixed system in presence of PEG 400 :

Conc. of PEG 400 % (w/v)	**Mole fraction of SDBS**											
	0.1				**0.5**				**0.9**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	-12.1	-11.0	-10.8	-11.5	-9.9	-8.8	-8.5	-8.4	-8.9	-8.3	-8.1	-7.9
0.1	--	-8.57	-14.90	-7.19	-7.04	-3.41	-5.78	-9.18	-6.31	-7.04	-7.48	-7.48
0.3	-13.51	-7.45	-5.53	-5.63	-6.93	-6.11	-4.37	-2.91	-6.12	-6.78	-7.25	-7.39
0.5	-8.17	-4.70	-11.05	-10.52	-8.47	-10.59	-7.90	-7.51	-6.22	-6.78	-7.30	-7.44
0.7	-7.17	-5.09	-5.25	-7.19	-4.28	-8.86	-3.57	-7.61	-6.01	-6.85	-7.27	-7.44

Table 65 : Interaction parameter (β^m) for SDBS / $C_{12}E_{10}$ mixed system in presence of sucrose :

Conc. of Sucrose % (w/v)	Mole fraction of SDBS											
	0.1				0.5				0.9			
	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C	35°C	40°C	45°C	50°C
0.0	-12.1	-11.0	-10.8	-11.5	-9.9	-8.8	-8.5	-8.4	-8.9	-8.3	-8.1	-7.9
0.1	-5.39	-6.28	-7.41	-5.63	-4.11	-7.98	--	-5.00	-6.53	-7.11	-7.33	-7.66
0.3	-5.98	-11.57	-3.37	-7.00	3.05	-2.45	-9.15	-3.19	-6.70	-7.03	-7.41	-7.59
0.5	-6.43	-9.98	-5.53	-8.69	-8.79	-2.66	-4.30	-1.97	-6.66	-7.08	-7.35	-7.65
0.7	-8.83	-6.88	-3.06	-10.40	-2.68	-4.18	-8.70	-10.47	-6.53	-7.06	-7.28	-7.58

Table 66 : Interaction parameter (β^m) for SDBS / $C_{12}E_{10}$ mixed system in presence of urea :

Conc. of Urea % (w/v)	**Mole fraction of SDBS**											
	0.1				**0.5**				**0.9**			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
0.0	-12.1	-11.0	-10.8	-11.5	-9.9	-8.8	-8.5	-8.4	-8.9	-8.3	-8.1	-7.9
0.1	-5.09	-1.84	-2.60	-4.41	-4.02	-4.09	-3.92	-3.72	-8.80	-8.86	-8.89	-9.03
0.3	-4.64	-5.08	-5.21	-3.53	-4.32	-4.42	-4.43	-4.42	-8.77	-8.87	-9.00	-9.07
0.5	-4.25	-4.78	-5.33	-2.59	-4.54	-4.71	-4.68	-4.71	-8.76	-8.86	-9.01	-9.06
0.7	-4.48	-4.69	-2.14	-2.43	-4.49	-4.46	-4.57	-4.67	-8.56	-8.69	-8.82	-8.88

$$\mu_{S.M} = \mu^{o}_{S,M} + (1 + \phi)\, RT \ln Y_M$$

ϕ is the micellar counterion dissociation and Y_M the surfactant mole fraction in micelles. Noting that $Y_M = 1$ for pure micelle and writing equations similar to above ones in presence of an additive A, one finally obtains.

$$\Delta G_{t(W,\, WA)} = \mu_{W,A} - \mu^{o}_{W}$$

$$= 2\, RT \ln \frac{CMC_W}{CMC_{W+A}} + (1 + \phi)\, RT \ln Y_M$$

Where $\Delta G_{t(W,\, WA)}$ represents the standard free energy of transfer of one mole of surfactant from aqueous phase to micellar pseudo phase in presence of additive A.

The mole fraction of additive Z_M within the micelle is defined by $Y_M = 1\text{-}Z_M$. If the mole fraction of additive solubilized is very small, $\ln Y_M = \ln (1 - Z_M) = -Z_M$. Assuming the distribution process, $Z_M = PZ_A$ where Z_A is the total solute mole fraction, P is the partition coefficient in mole fraction between micelles and water, then -

$$\Delta G_{t(W,WA)} = 2\, RT \ln \frac{CMC_W}{CMC_{W+A}} - (1 + \phi)\, RTPZ_A$$

For ternary solutions where two components are dilute with respect to third one, it has been shown[323] that any standard thermodynamic quantity may be expanded as a function of additive concentration in terms of both pairwise, triplet and higher order terms. Using the properties of cross differential derivatives in dilute solutions below CMC with respect to both additive, A and surfactant, then -

$$\frac{\delta\, \Delta G_{t(W,WS)}}{\delta\, m_S} = \frac{\delta\, \Delta G_{t(W,WA)}}{\delta\, m_A} = 2\, \omega g_{AS} + 6\, \omega g_{AAS} + \text{---------}$$

Where $\Delta G_{t(w,ws)}$ is the standard free energy of transfer of the neutral solute from the aqueous phase to the micellar phase, g_{AS} and g_{AAS} are pairwise and triplet interaction order terms and ω is the number of species, g_{AS} is equivalent to second virial coefficient specialized to a standard thermodynamic function.

The Setchenow constant is then defined by[93] -

$$g_{AS} = 2.303\ RT\ k^S_A\ m_A$$

Where k^S_A is the familiar Setchenow constant expressed in mole fraction scale and m_A is the molarity of the additive. In principle, this Setchenow constant may be obtained experimentally.

At the limit of small solute concentration one can write -

$$\log \frac{CMC_W}{CMC_{W+A}} = \frac{1}{2} \left[k^S_A + \frac{P(1+\phi)M}{2.303 \times 1000}\ m_A \right]$$

M is the molecular weight of water, CMC_W and CMC_{W+A} are the CMC in absence and presence of additive at concentration m_A. The above equation can be written in a generalized form -

$$\log \frac{CMC_W}{CMC_{W+A}} = K_M\ m_A$$

where K_M is a constant. The Setchenow constant k^S_A may be positive or negative and generally in case of salting-in-effect k^S_A is negative. This salting constant is evaluated from an empirical equation[323] -

$$k^S_A = 0.637 - 0.014\ n\ \{CH_2\} - 0.1464\ r$$

where n is the number of methylene groups in the surfactant aliphatic chain and r is the hard sphere diameter of the solutes, which is evaluated from vander Waals volumes as given by Bondi[324].

As mentioned before that if the mole fraction of solubilized additive is small, then RT ln Y_M = RT ln $(1-Z_M) = -Z_M$ RT. Assuming that, the penetration of the solute into the micelle is a linear function of its bulk mole fraction E.

$$\mathbf{- RT\ Z_M = -RT\ q\ E = \frac{RT}{1000}\ q\ M\ m_A}$$

where q is the ideal partition coefficient. The Setchenow equation takes the form[325] -

$$\mathbf{K_M = \frac{1}{2}\ [k^S{}_A + M\ q\ /\ 2.303 \times 1000]}$$

The r values calculated for PEG 400, sucrose and urea are 7.46, 8.04[326] and 4.70 A°[326] respectively. The r value for PEG 400 was calculated from the vander Waals increments of atoms or groups as given by Bondi[324]. The $k^A{}_S$ values thus calculated for all the systems were negative indicating a salting in effect in aqueous surfactant solution.

The K_M values calculated for various systems like SDBS, Myrj 45, $C_{12}E_{10}$ as well as SDBS / $C_{12}E_{10}$ mixed system in presence of PEG 400, sucrose and urea were all negative. Representative data of K_M for SDBS / $C_{12}E_{10}$ - additive systems are shown in Table 67.

The ideal partition coefficient q thus obtained using K_M and $k^A{}_S$ values tend to zero for all the systems. Such q value suggests that these additives do not penetrate the micelle i.e. the additives are not partitioned between the micelle and the solvent. This is generally observed in predominantly hydrophilic solutes as shown by CMC increase although PEG 400, and sucrose decrease the CMC of nonionic surfactant

Table 67 : The micellization constant (K_M) for SDBS / $C_{12}E_{10}$ mixed system in presence of PEG 400, sucrose and urea at different temperatures :

SDBS / $C_{12}E_{10}$	PEG 400				Sucrose				Urea			
	35°C	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**	**35°C**	**40°C**	**45°C**	**50°C**
9:1	-7.95	-1.62	-1.74	-1.26	-2.77	-2.99	-3.50	-2.16	-0.66	-0.59	-0.58	-0.60
5:5	-1.46	-1.33	-1.19	-1.71	-1.53	-2.15	-1.78	-1.53	-0.26	-0.38	-0.29	-0.21
1:0	-2.23	-2.12	-1.73	-1.27	-1.96	-1.84	-2.02	-3.09	-0.32	-0.35	-0.49	-0.46

initially. The variation of the CMC with the addition of these solutes may be entirely ascribed to the effect of these additives on the bulk solvent properties. Therefore, the additives by interacting both with the surfactant monomers induce a shift of the equilibrium between the micelles and surfactant monomers in favour of the latter. Since, these additives are non-penetrating ones i.e. do not penetrate into the micelle they can probably be assumed to locate themselves at the micelle-solvent interface.

i) NMR Spectroscopy :

The proton NMR spectroscopy was also used for the studies of SDBS / $C_{12}E_{10}$ mixed surfactant behavior. Fig. 25, 26 show the $C_{12}E_{10}$ spectrum and SDBS spectrum respectively. The peak assignments were done as reported earlier[327,328]. The changes in the chemical shifts on the gradual addition of SDBS to $C_{12}E_{10}$ was monitored. The spectra recorded for different mole ratios of SDBS / $C_{12}E_{10}$ are shown in Fig. 27-31. It is observed from the spectra that the oxyethylene proton signal shows marked changes on the addition of SDBS. Fig. 32 shows the changes in the chemical shift of the ethylene oxide signal against the SDBS mole fraction. It is observed that the polyoxyethylene signal shifts to higher magnetic field in presence of SDBS i.e. the extent of upfield shift depends on the SDBS mole fraction in the mixed system. Such upfield shift was observed earlier[329] also for anionic - nonionic surfactant mixture which has been ascribed to the interaction of polyoxyethylene chain with the benzene ring of anionic surfactant i.e. sodium p-octyl benzene sulfonate. However, in our studies no appreciable changes in the peak position due to phenyl protons near to alkyl chains was observed. The UV spectroscopy also did not show any change in the position of λ_{max} (220 nm for phenyl ring) in the mixed system.

An evidence for the interaction can be provided by the changes in the chemical shift of polyethylene glycol in D_2O shows a peak at 3.67 ppm corresponding to the resonance of ethylene oxide proton[330]. This moves up field at $\delta = 3.54$ ppm on addition of SDBS. Moreover, the phenyl proton shows a downfield shift from $\delta = 7.50$ ppm to $\delta = 7.57$ ppm. This is indicative of interaction between SDBS / $C_{12}E_{10}$.

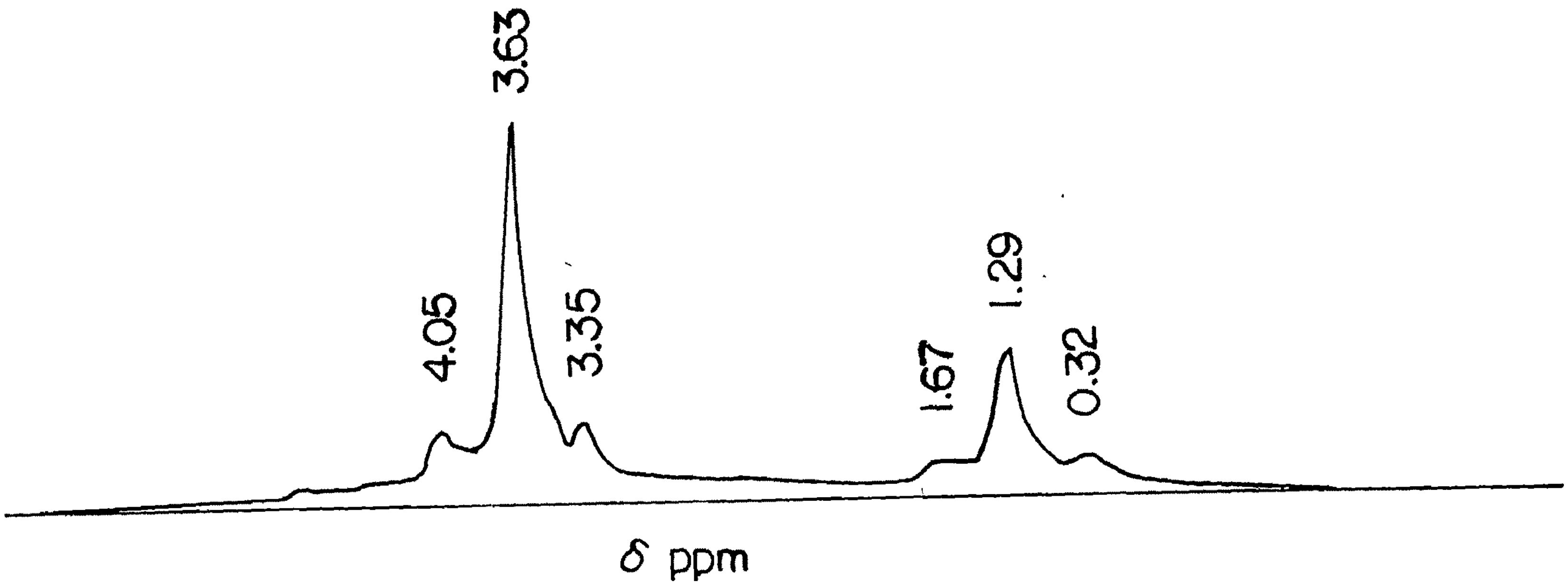

Fig. 25 : Proton NMR spectrum of $C_{12}E_{10}$.

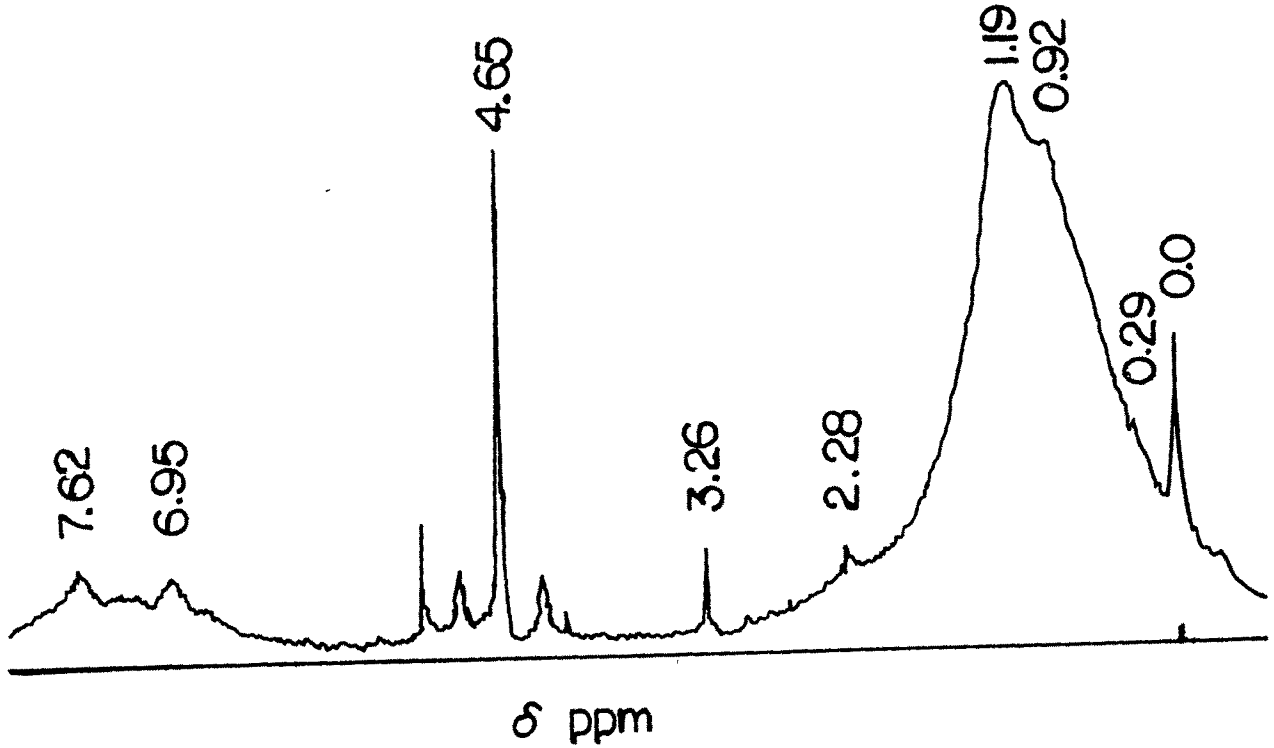

Fig. 26 : Proton NMR spectrum of SDBS.

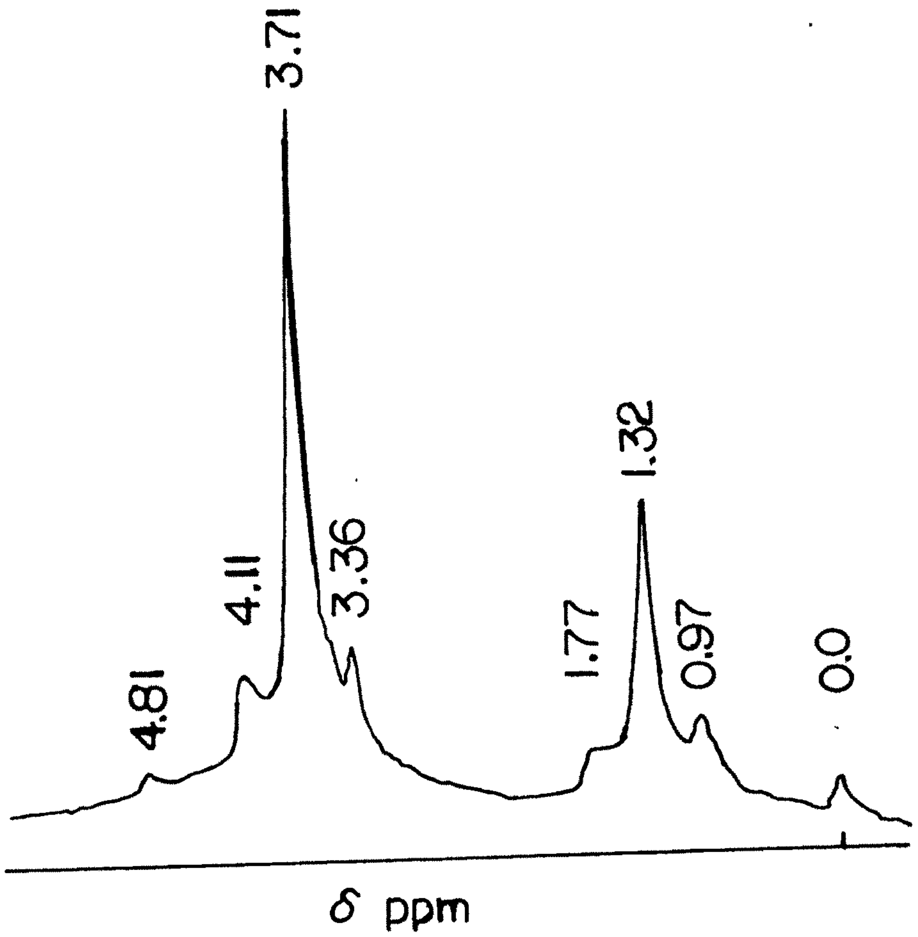

Fig. 27 : Proton NMR spectrum of 1:9 SDBS / $C_{12}E_{10}$.

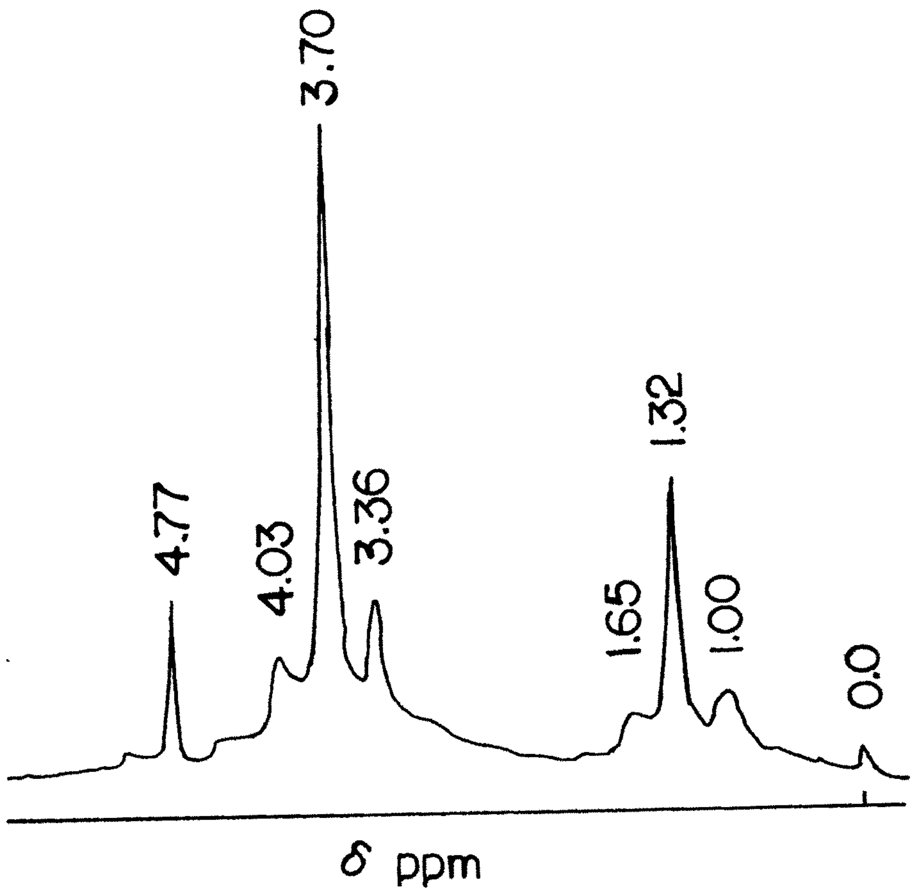

Fig. 28 : Proton NMR spectrum of 3:7 SDBS / $C_{12}E_{10}$.

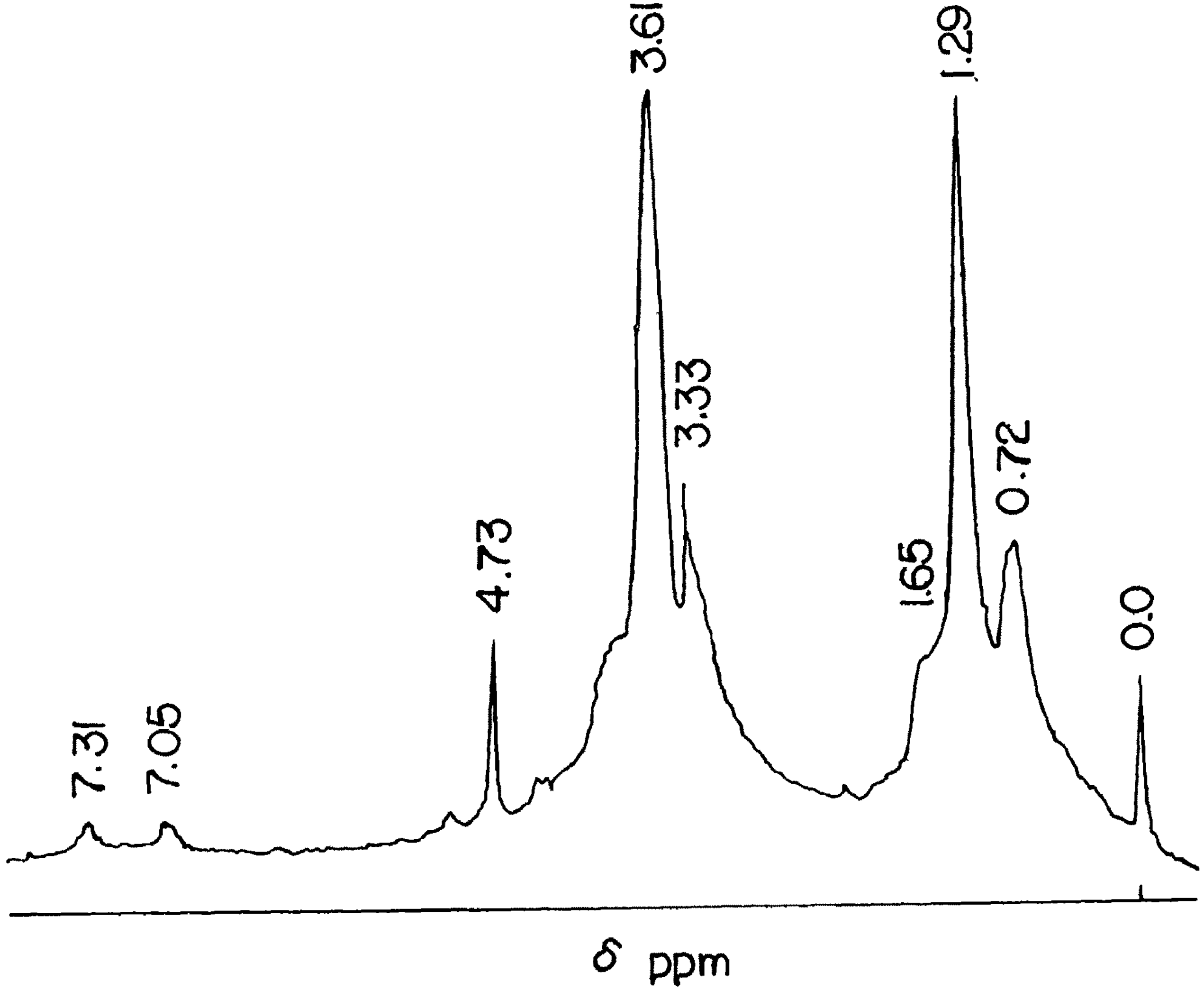

Fig. 29 : Proton NMR spectrum of 5:5 SDBS / $C_{12}E_{10}$.

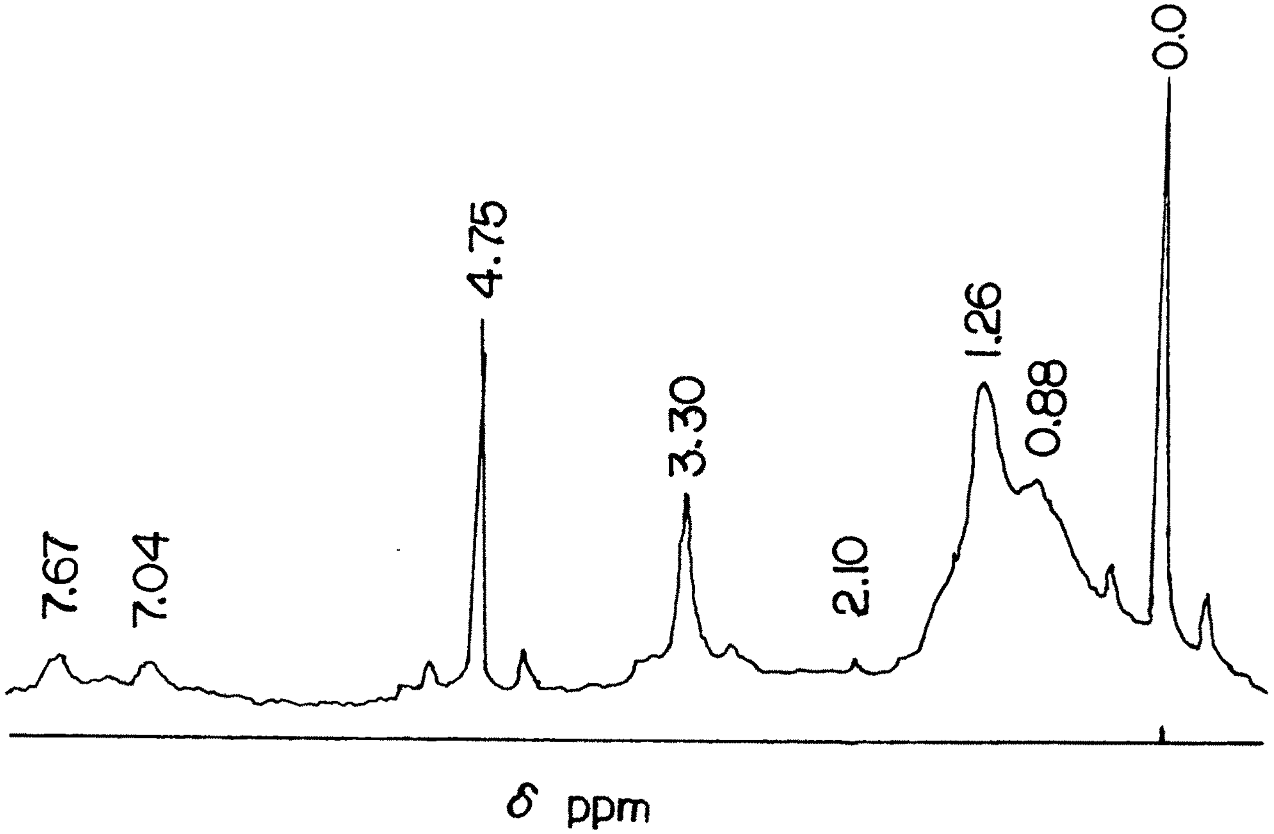

Fig. 30 : Proton NMR spectrum of 7:3 SDBS / $C_{12}E_{10}$.

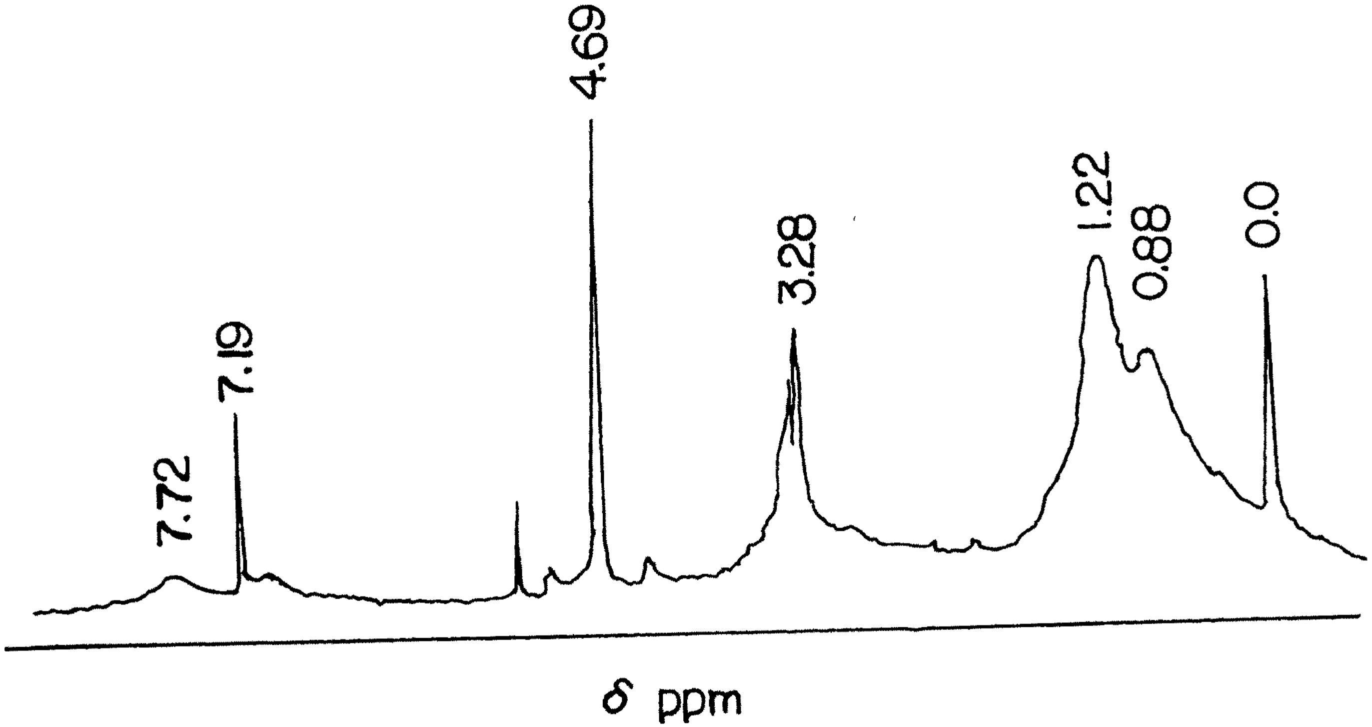

Fig. 31 : Proton NMR spectrum of 9:1 SDBS / $C_{12}E_{10}$.

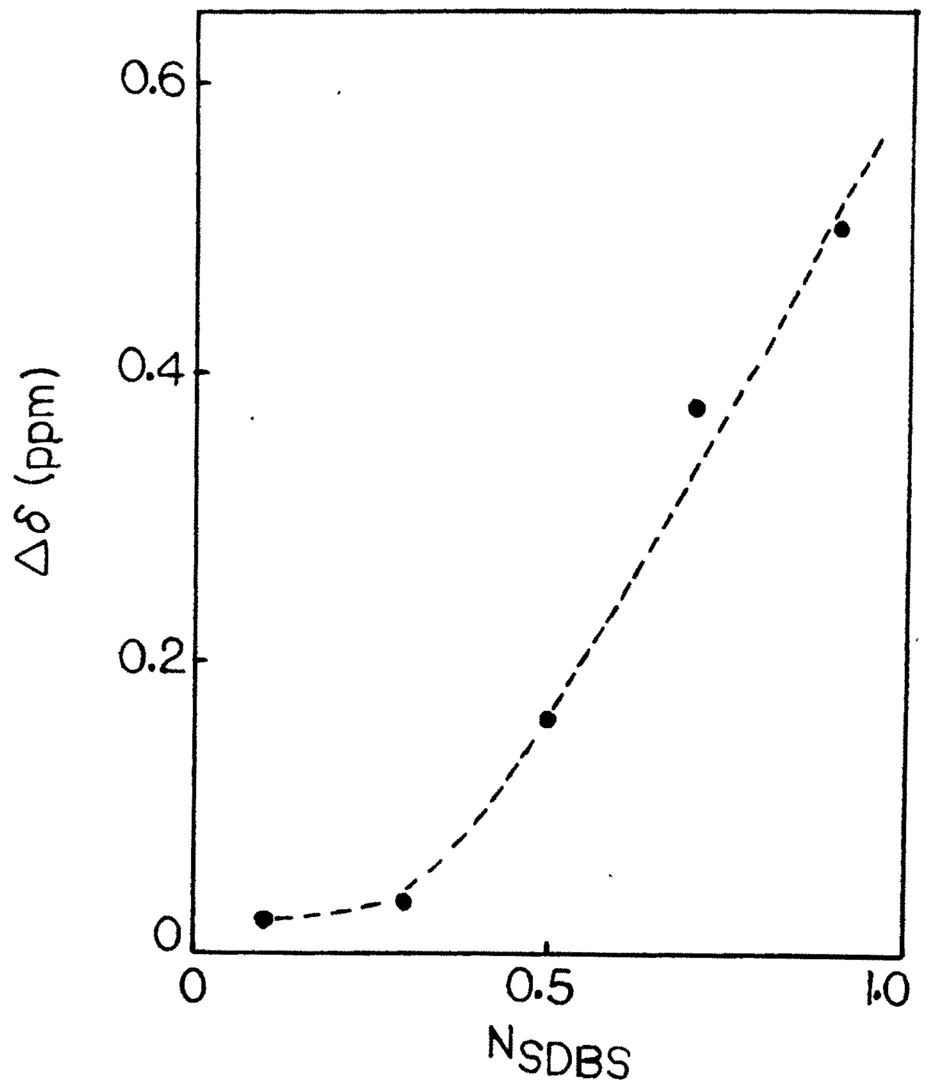

Fig. 32 : Plot of change in upfield shift of polyoxyethylene proton signal (Δδ ppm) against SDBS mole fraction.

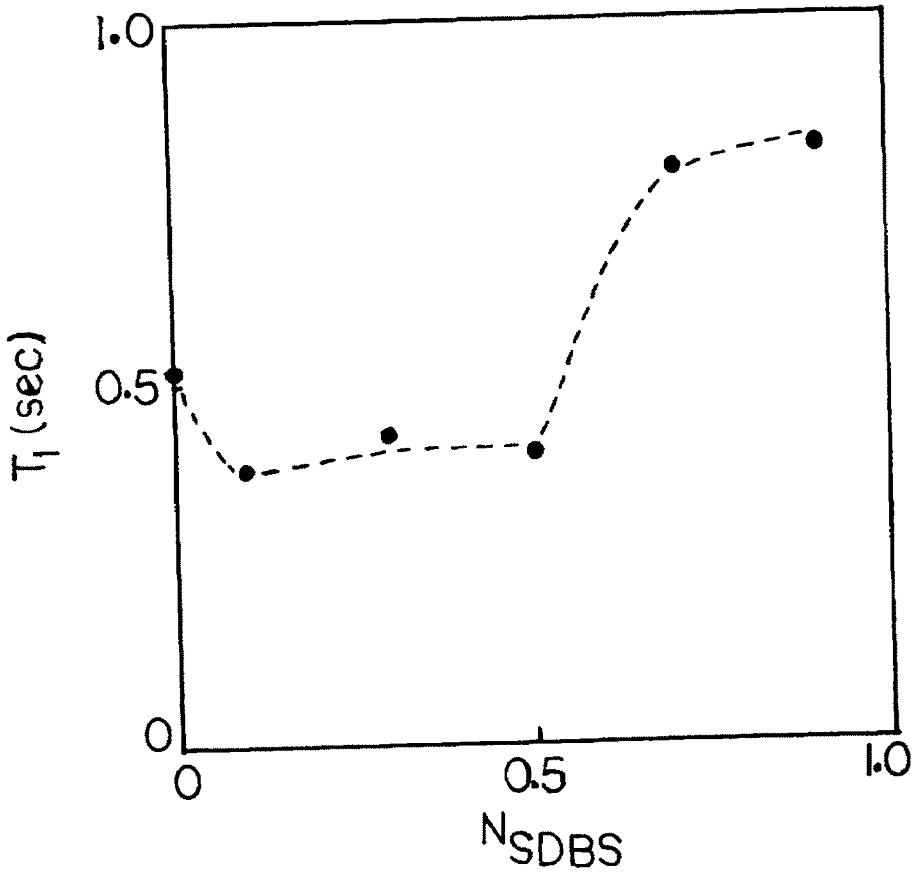

Fig. 33 : Plot of spin lattice relaxation time T_1 (sec) against SDBS mole fraction for SDBS / $C_{12}E_{10}$ mixed system.

The ^{1}H longitudinal relaxation time (T_1)was measured for this mixed system. Since the oxyethylene signal was sufficiently intense and well resolved and showed appreciable changes with SDBS, the T_1 measurements were done only for polyoxyethylene protons that resonate at $\delta = 3.60$ ppm. As the resolution of aromatic protons signal was poor at higher mole fractions of $C_{12}E_{10}$, the T_1 measurements were not done.

As shown in Fig. 33 the T_1 values initially decreases on very first addition of SDBS and remains almost constant upto SDBS = 0.5 and then increases considerably on further addition of SDBS. This can be rationalized to the restricted motion of oxyethylene chains at lower mole fractions of SDBS in comparison to pure $C_{12}E_{10}$. On further addition of SDBS the micellar structure loosens up due to mutual coulombic repulsions of the ionic heads in the mixed micelle.

CONCLUSIONS

The critical micelle concentrations (CMC) of nonionic Myrj 45, $C_{12}E_{10}$, ionic SDBS and SDBS / $C_{12}E_{10}$ mixed surfactant system were determined. The effect of additives like PEG 400, sucrose and urea on these systems were studied. The CMC of nonionics decreased whereas increased in case of ionic with rise in temperatures as expected. The SDBS / $C_{12}E_{10}$ mixed systems showed an increase with increase in temperature suggesting that mixed micelles were ionic in nature. Both sucrose and PEG 400 promoted the micelle formation in case of nonionic Myrj 45 and $C_{12}E_{10}$. However an increase in CMC was observed for SDBS and SDBS / $C_{12}E_{10}$ mixed system. Urea, a well known protein denaturant and potential water structure breaker, increased the CMC for all the systems, a fact ascribed to the greater monomer stability in presence of urea.

The standard free energy of micellization (ΔG°_m) for all the systems studied were found to be negative indicating a spontaneous micelle formation. The minimum in ΔG°_m - N_{SDBS} plot at $N_{SDBS} = 0.1$ indicates mixed micelle stability. It should be noted that the micelle formation was more spontaneous in the absence of PEG 400, sucrose and urea for SDBS / $C_{12}E_{10}$ mixed system. The micellization process was endothermic for nonionic surfactants in pure water and exothermic for mixed system and in presence of additives. The entropy of micellization (ΔS^{o}_{m}) was positive for all the systems studied. The overall micellization has been attributed to various antagonistic features. The enthalpy - entropy compensation effect was observed for all the solvent systems with an isostructural temperature ~ 300 K. The $\Delta\Delta H^{otr}_{m}$ values were all negative indicating the surfactant hydrophilic group additive interactions. A maximum observed in transfer heat capacity of micellization ($\Delta\Delta C_{p}{}^{tr}{}_{m}$)-additive concentration is ascribed to micellar structural transition. The Γ_{max} and A_{min} values indicate a marked effect of these additives on surfactant adsorption. The positive value for the 'work of transfer' in all cases suggests a positive change upon adsorption than upon micellization.

The micellar aggregation number (N_{agg}) decreases for all surfactant systems in presence of additives. The effect is attributed to the hindrance in the micelle formation due to the presence of additives at the micellar hydrocarbon water interface.

The ideal partition coefficient measuring the partition of these additives between the solvent bulk and the micelle suggests that these additives being non-penetrating ones their effect on the variation of CMC can be entirely ascribed to the changes in the solvent structure. The negative β^{m} values indicate an attractive interaction between SDBS and $C_{12}E_{10}$ in the mixed micelle.

The ^{1}H NMR studies indicate the interaction between the oxyethylene - benzene ring of nonionic $C_{12}E_{10}$ and ionic SDBS. In conclusion, a marked effect on the physicochemical properties in presence of these additives is observed.