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Micellization and Related Behavior of Sodium Dodecylsulfate in Mixed Binary Solvent Media of Tetrahydrofuran (Tf) and Formamide (Fa) with Water: A Detailed Physicochemical Investigation

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Abstract

Detailed aggregation behavior of sodiumdodecyl sulfate (SDS) in tetrahydrofuran (Tf)/Water (W) and formamide (Fa)/Water (W) media at varied volume percent compositions has been investigated. Surface tension (ST), conductance (Cond), Viscosity (Visc), isothermal titration calorimetry (ITC), nuclear magnetic resonance (NMR) and small angle neutron scattering (SANS) were used in the study. The presence of the nonaqueous solvents affected the critical micelle concentration (CMC) of SDS, the counter-ion binding of the micelle, the energetics of the air/water interfacial adsorption and micellizattion of the amphiphiles in the bulk, the ion-association (ion-pair, triple-ion, quadruple, etc between Na^+ and DS^- ions) as well as the weakly soluble (aggregation less) amphiphile solution. Tf has been observed to produce a "dead zone" or "non-micelle formation zone" in the mixed Tf/W domain of 10-40 v%. Fa influenced the SDS aggregation up to 70 v%, at higher proportions (below the Krafft temperature (K_T)), instead of micelle, "randomly arranged globular assembly" (RAGA) was formed. The correlation of the standard free energy of micellization (ΔG_m^0) with different solvent parameters (1) dielectric constant (ε), (2) viscosity (η_0), (3) Reichardt parameter (E_T30), (4) Gordon parameter (G), and (5) Hansen-Hildebrand hydrogen bonding parameter (δ_h) has been attempted. It has been found that δ_h produced a master correlation between ΔG_m^0 and δ_h for different binary mixtures such as Tf/W, Fa/W, Ml/W and Dn/W.

1. Introduction:

The self-aggregation of amphiphilic substances occurring both in aqueous and non-aqueous media[1,2] is primarily guided by the hydrophobic effect.[3] Working with hydrazine for water, Evans et al.[4,5] have concluded that the specific characteristics of water may not be vital for promoting amphiphile self-assembly. Elaborate attempts have been made to understand the role of non-aqueous solvents on the self-assembly of amphiphiles in terms of different factors viz, permittivity, cohesive energy, fluidity, hydrogen bonding ability, viscosity, etc. Such investigations have scopes in the uses and applications of surfactants, lipids and polymers in the areas of chemistry, pharmacy and medicine.[6-9] Studies on the micelle formation of amphiphiles in mixed solvent media of water and organic solvents are frequently found in literature. They comprise partial replacement of water by water soluble non-aqueous solvents allowing the assessment of the amphihilic processes over a wide range of compositions. Towards this end, potential studies with ionic, nonionic and zwitterionic surfactants in mixed aquo-organic solvent media have been conducted.[10-26]

Studies on micellization of ionic and nonionic surfactants, as well as polymers in pure formamide (Fa) are available in literature.[27-41] It has been shown that the driving force for the initial solvophobicity towards the amphiphiles has similarities with the hydrophobic effect that arises from the large cohesive energy of the solvent like water. Ray et al.[2,3] (decades ago) evidenced micelle formation of ionic surfactants in Fa but not in N, N-dimethylformamide (DMF) which is equally polar like the former. Gopal et al.[27,28] found similar behavior for other surfactants, whereas Singh et al.[29] claimed that micelles of SDS and CTAB (cetyltrimethylammonium bromide) were not only formed in Fa and N-methyl acetamide (NMA) but also in dimethyl sulfoxide (DMSO) and DMF. It was shown later that some kind of "solute-solvent assemblies" instead of true micelles were formed in these solvents.[30] Micellization of SDS in Fa was claimed from tensiometry[31] and Raman spectroscopy experiments.[32] In the CTAB-Fa system at 333K spherical micelles were identified from multifield NMR relaxation study.[33] The ^2H relaxation data evidenced nondectable SDS micelles in Fa at 289K[34] in agreement with self-diffusion data.[35] Instead, a sequence of liquid crystalline phases (hexagonal-cubic-lamellar) was evidenced at higher concentration and elevated temperature.[36] ^2H-NMR study of SDS in Fa at 333K (above its Krafft temperature, K_T = 330K) revealed moderate increase in micelle size with increasing [SDS]. Below K_T a metastable cubic phase was detected; self-diffusion measurements demonstrated that the cubic phase was micelle-like.[37] At room temperature, well below the K_T, the surfactant has limited solubility of about 7-8 wt% in Fa. It has been demonstrated by several experimental techniques that micelle formation of SDS does not occur within this solubility limit.[30,33,34] From small-angle neutron scattering (SANS) study Perche et al.[38] showed formation of micelle above the K_T of SDS in Fa following a multiple equlibria model rather than pseudophase model. Recently, Yue et al.[39] investigated lyotropic liquid crystalline phase formation of phytosterol ethoxylate surfactant (BPS-10) in Fa. Although surfactant self-aggregation has been studied in aquo-organic solvent media, only a few papers dealt with the effect of progressive addition of Fa in water on the process. Warnhein et al.[40] studied the behavior of CTAB in Fa-W medium. A lack of general correlation between the dielectric constant of the solvent and the CMC and hence the aggregate size was observed. Moya et al.[20] have studied the effect of the presence of Fa (up to 50 v%) on the aggregation of TTAB (tetradecyltrimethylammonium bromide), DTAB (dodecyltrimethylammonium bromide), SDS and Triton X-100 (t-butylphenoxypolyoxyethylene (9.5)ether) in aqueous medium, and correlated the free energy of micellization with the Gordon parameters(G). Alexandridis et al.[41] have also reported SANS results on the micelle formation and structure of a block co-polymer in several mixed solvent media including Fa-W. Nevertheless, only a few reports on the effect of tetrahydrofuran (Tf) on the micellization of different surfactants appear in literature.[42,43] It may be added that Tf has water structure making and breaking properties and produce micellization of CTAB and TTAB up to 15 and 20 v% of Tf in water,[43] respectively at 303K. More studies in this area are wanted.

Water soluble non-aqueous solvents have been found to lower the critical micelle concentration (CMC) of surfactants at low concentration by their solvophobicity, whereas at moderate to high concentrations they increase CMC by way of their increased solvophilicity towards the surfactants as well as breakdown of water structure.[15,26] In previous studies, a minimum concentration of 10 w% of different non-aqueous solvents have been used to study amphihile self-aggregation, and physico-chemically correlate the process with a number of solvent parameters viz, viscosity(η_o), permittivity(ε), dipole moment(μ), $E_T(30)$, Gordon parameter(G), Hansen-Hildebrand parameter (dispersion, δ_D; polar, δ_P; hydrogen bonding, δ_h), polarity index (π^*), and Gutman donor number (DN), etc.

Co-solvents are known to interact with surfactant monomer, water and micelles, and consequently shift the CMC.[44,45] The degree of interaction depends on their structure, composition, functional groups present in the molecule, types of surfactant they interact with, etc. In view of the above, we have investigated the effect of two solvents of opposite categories, one Tf (weakly polar aprotic, having low cohesive energy density, and low hydrogen bonding ability with water), and the other Fa (polar protic having high cohesive energy density, and high hydrogen bonding ability) on the self-aggregation of SDS in their binary mixtures with water. A large number of proportions of both Tf and Fa from 0 to 100 vol% (v%) were used to obtain information on the quality of the mixed solvents on the self-association process of SDS, and structural changes of the aggregates. The CMC, counter-ion binding, energetics of the process, nature of interaction of SDS with the solvent molecules, micelle forming and non-micelle forming zones, and ion-association (between Na^+ and DS^-) have been attempted to evaluate using conductometry, tensiometry, calorimetry, viscometry, and NMR methods. Morphologies of the aggregates have been also determined from SANS measurements. In a previous study[12] we had assessed the role of low and high polar mixed solvents 1,4-dioxane-water (Dn-W) medium and high polar mixed medium methanol-water (Ml-W) on the self-assembly of SDS. The Tf-W mixed solvent system herein used was low and high polar mixed solvent system but Fa-W was a mixed system of two high polar solvents. Elaborate study on surfactant behavior in mixed solvent systems herein presented was hardly conducted in the past.

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium dodecylsulfate was 99% pure of AR grade product of SRL, India. The nonaqueous solvents tetrahydrofuran (Tf) and formamide (Fa) were GR and AR grade products of SPECTROCHEM (India), respectively. The deuteriated tetrahydrofuran (Tf) and formamide (Fa) were obtained from Sigma Aldrich (USA). The SDS (for NMR) and other NMR reference standards 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (Z97%, DSS) and deuterium oxide (D_2O) (Z99.9 atom% D) were purchased from Aldrich. Doubly distilled conductivity water (specific conductance, $\kappa = 2 - 3\ \mu\mathrm{S\,cm^{-1}}$ at 303 K) was used in the study.

2.2 Instruments and methods

2.2.1 Conductometry

A conductometer (EUTECH, Singapore) was used for conductance measurements placing the cell (cell constant = 1 cm^{-1}) in a double-walled glass container at 303 K maintained by a Hahntech, DC-2006 circulating bath with an accuracy of ± 0.1 K. A concentrated surfactant solution was progressively added to 6 ml of mixed (water-organic) solvent using a Hamilton microsyringe. The results were graphically processed to evaluate CMC and counter ion binding (β) in the usual way.[12]

2.2.2 Isothermal Titration Calorimetry (ITC)

An OMEGA, ITC microcalorimeter (Microcal, USA) was used for thermometric measurements. A concentrated solution of SDS (~15 times CMC taken in a 325 μl microsyringe) was injected for a duration of 30s into 1.325 ml of solvent in the calorimetric cell at equal time intervals (210s) in multiple steps (32-50 additions) under constant stirring (350 rpm) condition. All measurements were taken under thermostated conditions (303 ± 0.01 K) maintained by a Nesleb RTE 100 circulating water bath. The heat released or absorbed at each step of dilution of surfactant solution in either water or mixed solvent was recorded and the enthalpy change per mole of injectant was calculated with the ITC Microcal Origin 2.9 software. The reproducibility was checked from repeat experimentations. The procedure for the evalution of CMC and enthalpy of micellization (ΔH^0_m) from the thermograms was as reported.[46]

2.2.3 Tensiometry

Surface tension measurements were taken with a calibrated du Noüy tensiometer (Krüss, Germany) by the ring detachment technique. A volume of 6 ml of solvent was taken in a double-wall jacketed container placed in a thermostatted water-bath (accuracy, ±0.1 K) at 303K into which a stock solution of SDS of desired concentration (~ 10-15 times CMC) was stepwise added with a Hamilton microsyringe as required (allowing ~ 10 min for mixing and thermal equilibration). The detailed procedure of surface tension measurements has been reported earlier.[12] The measured surface tension (γ) values were accurate within ± 0.1 mN m^{-1}.

2.2.4 Determination of Krafft Temperature

The Krafft temperatures (T_K) of SDS in pure Fa as well as in mixed solvent (Fa-W and Tf-W) media were determined by dissolving different amounts of the surfactant in the medium of a fixed solvent composition. Both stirring and slow heating were applied for dissolution. The solutions were then kept in test tubes in a freezer overnight at ~ 253K. They were taken out and were then slowly heated and the solutions formed were continuously stirred to find the points of clarity, and the corresponding temperatures were noted. The concentrations of SDS are plotted against the temperatures of their solubility states. Two distinct linear courses were observed. Junction point was taken as the T_K. The standard deviations of the measurements were ± 3%. SDS was very weakly soluble in pure Tf, hence its T_K in pure Tf could not be measured. T_K values of SDS in solvent compositions of 50, 70 and 90 v% Fa and 90 v% Tf in water were determined.

2.2.4 Nuclear Magnetic Resonance (NMR)

The Nuclear Magnetic Resonance (NMR) experiments were done (at 298 K) in an ECA-500 JEOL spectrometer operating at 500MHz. The SDS proton self-diffusion coefficient (D) measurements were taken in SDS/D_2O, SDS/Tf/D_2O and SDS/Fa/D_2O mixtures of different compositions with varied [SDS], while Tf/Fa at a fixed concentration in the Tf-W and Fa-W mixtures. All diffusion measurements were taken with the bipolar pulse pair longitudinal encode-decode (BPPLED) pulse sequence.[47] For the diffusion measurement, the experimental variable gradient duration (Ω) and diffusion time (Δ) were fixed at 6 ms and 100 ms, respectively, whereas the amplitude of the gradient (g) were varied from 20 to 280 mT / m in 15 steps. In order to obtain reasonable signal to noise ratio, a line broadening of 5 Hz was applied to each 'free-induction-decay' (FID) and Fourier transformed during diffusional analysis. The diffusion coefficients were obtained by nonlinear fitting of the experimental data to the Stejaskal-Tanner equation;[48] $I = I_0 e^{-kD}$ where, I_0 is the peak intensity in the absence of gradient pulses, and the parameter $k = (\gamma_n \, \Omega \, g)^2 \, (\Delta - \Omega/3)$ where, γ_n is the gyromagnetic ratio and D is the translational self-diffusion coefficient. A single-exponential decay was observed for all the samples, as observed from plots of intensity versus g^2 and the corresponding estimated error in D was within ± 5%. The self-diffusion coefficients of all SDS protons were utilized in the diffusional analysis.

^{13}C chemical shift measurements were also taken on separate samples prepared for probing the preferential solubilization site of Tf/Fa in SDS. 1 M DSS in D_2O in a coaxial tube was taken as an external reference during ^{13}C chemical shift studies. The resonance position of methyl carbons of DSS was arbitrarily considered as zero and other resonances are quoted relative to this.

The ^{23}Na spin-lattice relaxation rate ($R_1 = 1/T_1$) measurements were taken for SDS/Tf/D_2O mixtures with different compositions as a function of [SDS] using inversion-recovery pulse sequence. The ^{23}Na Magnetization recovery profile was observed to be single exponential. The R_1 data were computed using a nonlinear three parameter fit with an estimated error of ±2%. All data processing was done with the aid of Jeol-Delta-NMR software.

2.2.5 Viscometry

An Ubbelohde viscometer of 103.6s average flow time for 10 ml water at 303 K was used in the study. The solvent solutions (10 ml) without and with SDS were taken in the viscometer (placed in a thermosatted water bath of accuracy ± 0.1 K) and the flow times were measured after thermal equilibration. The concentration of the SDS solution in the viscometer was varied by stepwise addition of concentrated solution with the help of a Hamilton microsyringe. Errors in measurements were within ± 0.5%. In each set measurements were duplicated and their mean values were recorded and used.

2.2.6 Small Angle Neutron scattering (SANS)

SANS experiments were performed with a diffractometer at the Dhruva reactor, Bhabha Atomic Research Centre, Trombay, Mumbai (India). The diffractometer makes use of a beryllium oxide filtered beam with a mean wave length ($\lambda = 5.2$ Å). The angular distribution of scattered neutrons was recorded using a one dimensional position sensitive detector (PSD). The accessible wave vector transfer ($q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) and the range of the diffractometer was 0.017-0.35 $Å^{-1}$. The PSD allowed simultaneous recording of data over the full q. The samples were held in a quartz sample holder of 0.5 cm thickness. The experimental temperature was kept fixed at 303 K. Measured SANS data were corrected and normalized to absolute units (as cross-section per unit volume) using standard procedure.[49]

3. RESULTS AND DISCUSSION

3.1 Micelle and Related Parameters:

Knowledge of Krafft temperature (T_K) of a surfactant in a solvent is a necessary consideration in the study of its self-aggregation. As per report,[31] $T_K^{SDS}(w) = 289K$. But T_K of SDS in pure Fa is 328-330K[31]; in Fa-W medium it is expected to be $< 330K$. We have determined the T_K of SDS at 50, 70 and 90 v% of Fa-W. The results are presented in Figure S1(A). T_K of SDS at the above percentages of Fa are 298.3, 305.2 and 316K, respectively. The experimental temperature in this study was 303K. Up to 50 v% of Fa in water T_K of SDS was less than 303K; at 70v% of Fa, the T_K value was marginally higher than 303 K, and at 90 v% and above T_K was reasonably higher than 303K. Therefore, SDS aggregates (if any) in such mixed Fa-W media (~70 v% and above) were not micelles (probably some kind of undefined aggregates). In the following discussion, these T_K related facts will be further considered. SDS is practically insoluble in pure Tf. We determined T_K of SDS in 90 v% Tf-W medium to be 305.7 K(Figure S1B). Therefore at lower v% of Tf, the T_K of SDS is expected to be < 303K (the experimental temperature of the present study).

Conductometry, calorimetry, and tensiometry methods were used to determine (i) the critical micelle concentration (CMC), (ii) extent of counter-ion binding (β) to micelles, (iii) standard Gibbs free energy of micellization (ΔG_m^0) , (iv) standard enthalpy of micellization (ΔH_m^0), (v) maximum relative surface excess (Γ_{max}) of the surfactant (SDS) at the air/solution interface at CMC, and (vi) the maximum area per anion monomer of SDS at the interface (A_{min}) at 303 K. In the wide spread of component proportions in the binary solvent mixtures, micelle and non-micelle forming zones have been identified together with the zone of ion-association.

Conductometric plots (equivalent conductance (Λ) vs $\sqrt{C}$ (C = [SDS] in mM) in both tetrahydrofuran-water (Tf-W) and formamide-water (Fa-W) media at different volume percents (v%) are exemplified in Figure 1 A and B, respectively. The initial sharply declined breaks in the plots were taken as the CMC points which changed with changing v% of the nonaqueous solvents. It was observed that above 10 v% of Tf, the nature of the Λ vs $C^{1/2}$ plots produced upward trends; formation of CMC was not supported. For Fa-W system, above 70 v% of Fa, the nature of the decline in Λ was without reasonable inflection suggesting the absence of formation of micelle of SDS in the medium.

Calorimetric enthalpograms (ΔH vs [SDS] plots), where, ΔH = enthalpy of dilution of a concentrated solution of SDS) also revealed sigmoidal dependence suggesting micelle formation (inflection point = CMC; difference between the two asymptotes = ΔH_m^0) again up to 10 v% of Tf and 70 v% of Fa presented in Figure 2 A and B. The enthalpy courses were radically different at higher v% of both (which has been discussed in a different perspective in section 3.3).

Tensiometric isotherms also corroborated the above findings, up to 10 v% of Tf sigmoidal courses with distinct breaks in the γ (surface tension) vs log[SDS] plots identified the start of the CMC. Higher proportions of Tf (20 and 30 v%) produced non-micelle forming isotherms (Figure 3A). But in Fa-W medium, distinct breaks akin to CMC formation were observed even at v% (70-100).

The results are presented in Table 1 along with the average CMC(CMC$_{ave}$) and the extent of counter-ion binding (β) determined in the usual way and shown in the foot note 'b' of the table. It was found that the CMC of SDS declined with increasing concentration of Tf in water up to 6 v% and then increased whereas that in Fa-W medium decreased at 1 v% of Fa and then increased. The presence of Tf caused solvophobicity towards SDS and reduced the CMC whereas Fa imparted such an effect just at 1 v% then solvophilicity and caused increase in CMC. In our earlier report,[12] it was shown that dioxane (Dn) and methanol (Ml) produced solvophobicity up to 4 v% in water making an initial decline in CMC of SDS; at higher v% both the solvents were solvophilic towards SDS.[15,20] The behavior of Tf in water was different from that of both Dn and Ml as well as Fa. The solvophobicity of the furan moiety of Tf towards SDS enhanced the molecular association of SDS up to 10 v%; increased polarity (dielectric constant, ε) of the Fa-W medium caused increased CMC of SDS up to 50 v% and above (~70 v%). Fairly increasing viscosity (complementary of increased solvent structure) also supported easier assembly formation in Tf-W medium which was only marginal in Fa-W medium (cf Table S1). At higher v% of Tf (>10v%) and Fa (>60 v%), conductance, calorimetry and NMR methods produced inflections in the profiles of SDS which were different from the CMC forming courses. Ion-association, aggregate formation other than normal micelle were considered to arise in solution. These are discussed in section 3.3.

The counter-ion (Na$^+$) binding extent to the micelle in the mixed solvent media was found to decrease with increasing v% of both Tf and Fa; the rate of decrease was more with Tf addition than Fa. The magnitude of β depends on the charge density on the ionic micelle which is related with the micelle size or the aggregation number ($\bar{n}$). It was reported in a previous study[12] that $\bar{n}$ of SDS micelle decreased with the addition of both Dn and Ml in water making β to decrease. We have determined $\bar{n}$ of the SDS micelles in aqueous Tf and Fa by SANS (cf. Table 5, Section 3.4.2), and found that $\bar{n}$ declined with increasing concentration of both Tf and Fa in the aqueous medium (Table 5), and the rate of decline was more in Tf-W than in Fa-W. The decreased micelle size ended up with reduced surface charge and decreased β ($\beta_{\mathrm{Tf-W}} < \beta_{\mathrm{Fa-W}}$). Low polar Dn,[12] and Tf decreased β more than Ml and Fa. A first hand comparison shows that at 10 v%, the CMC, β and $\bar{n}$ produced by Tf were all lower than those produced by Dn in the mixed solvent media, excepting ε (which were nearly equal). At 50 v%, in all counts Fa surpassed Ml save $\bar{n}$.

3.2 Energetics of micellization and interfacial adsorption

The observed CMC and β values in addition to enthalpy of micellization ($\Delta H_{\mathrm{m}}^{0}$), and tensiometric results were used in the calculation of energetic and other parameters. The results are presented in Table 2. The maximum Gibbs surface excess at CMC ($\Gamma_{\max}$) of the surfactant (relative to water) at the air/solution interface was evaluated from the γ vs logC plots using the Gibbs adsorption equation shown in the footnote 'b' and 'c' of the table. Two degree polynomial equation was used to determine the dγ/dlogC at CMC from the first derivative of the relation, $\gamma = \mathrm{A} + \log\mathrm{C} + \mathrm{B}(\log\mathrm{C})^{2}$. $\mathrm{A}_{\min}$ (minimum area per surfactant molecule of the Gibbs monolayer) value was found from the relation, $\mathrm{A}_{\min} = \dfrac{10^{18}}{\mathrm{N}\Gamma_{\max}}$. The relation, $\Delta G_{\mathrm{m}}^{0} = (1+\beta)\,\mathrm{RT}\ln\mathrm{X}_{\mathrm{CMC}}$ (CMC expressed in mole fraction) was used for the estimation of $\Delta G_{\mathrm{ad}}^{0}$ from Rosen and Aronson formulation,[50] $\Delta G_{\mathrm{ad}}^{0} = \Delta G_{\mathrm{m}}^{0} - \Pi\,\mathrm{N}\,\mathrm{A}_{\min}$ (where, Π is the surface pressure at CMC, and N is the Avogadro number). On a comparative basis, $\Gamma_{\max}^{\mathrm{Tf-W}} < \Gamma_{\max}^{\mathrm{Fa-W}}$, and both declined with increased concentration of the non-aqueous solvents in the mixture. The rate of decline of γ with logC was more in Fa-W medium than in Tf-W medium; the slope $\left(d\gamma/d\log C\right)_{\mathrm{Fa-W}} >> \left(d\gamma/d\log C\right)_{\mathrm{Tf-W}}$, which made $\Gamma_{\max}^{\mathrm{Tf-W}} < \Gamma_{\max}^{\mathrm{Fa-W}}$. At equal v%, Fa produced more molecules in solution than Tf (cf. Table 1), which was felt also by the interface. The declining trend of $A_{\min}$ with increasing v% of both Tf and Fa caused from the increasing trend of $\Gamma_{\max}$. Reduction of the amphiphile population at the interface made concomitant increase in $A_{\min}$. Increasing site occupation by the surface active Tf and Fa at the interface competed with SDS making its interfacial population lower resulting the observed trends in $\Gamma_{\max}$ and $A_{\min}$. The surface excess of SDS at CMC ($\Gamma_{\max}$) by definition was relative to the zero surface excess of the mixed medium at the interface. In comparison with the $\Gamma_{\max}$ of SDS in water ($\Gamma_{\max}^{\mathrm{W}}$), the excess in the mixed solvents were all lower, and the difference increased with increasing concentration of both Tf and Fa because less room was provided to SDS at the interface by the presence of the surface active nonaqueous molecules.

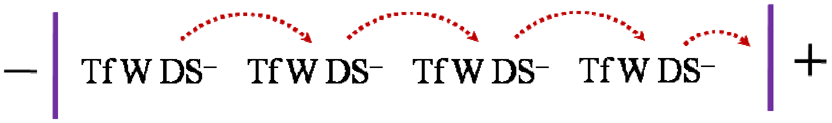
The $\Gamma_{\max}$ of SDS in water was 2.63x10^{-6} mol m^{-2}. At a comparable v% (say 10 v%), in Tf-W and Fa-W media the $\Gamma_{\max}$ were 0.93 and 1.76x10^{-6} mol m^{-2}, respectively. The $A_{\min}$ of SDS in water was 0.63 nm^{2} molecule^{-1}. In Tf-W and Fa-W media the corresponding $A_{\min}$ were 1.79 and 0.94 nm^{2} molecule^{-1}, respectively. The $\Gamma_{\max}$ thus decreased by 35.4 and 66.2 % in Tf-W and Fa-W medium, respectively, whereas the increased $A_{\min}$ were 64.9 and 33%. Thus, the decreases in surface population of SDS in the two media at 10 v% were 64.6 and 33.8%, respectively.

The energetic parameters ΔG_{m}^{0}, ΔG_{ad}^{0}, ΔH_{m}^{0} and ΔS_{m}^{0} are all standard state values. The trend in ΔG_{m}^{0} (Tf-W) became less spontaneous with increasing [Tf] in the medium. The trend was practically the same in the Fa-W medium; the ΔG_m^0(Fa-W) values were available up to 70 v%. ΔG_{ad}^0 found from Rosen and Aronson relation[50] slowly increased with increasing of both Tf and Fa content in the medium; the results (as expected) were more negative than ΔG_m^0. The ΔH_m^0 became more exothermic by the increasing presence of Tf in water; in Fa-W medium ΔH_m^0 formed a minimum at 30 v% (or 0.163 X_{Fa}) then increased forming a plateau. A change in the environment beyond 30 v% was envisaged. The standard entropy of micellization (ΔS_m^0) were all positive and high, and declined with increasing Tf and Fa content; after 30 v% Fa, ΔS_m^0 nearly came to a hault parallel to the behavior of ΔH_m^0. A ΔS_m^0-ΔH_m^0 compensation behavior was found valid with compensation temperature of 130.2 K and 99.1 K for Fa-W and Tf-W mixed solvents, respectively (Figure S2).

3.3 Anomalous physicochemical behavior of SDS at higher concentration of Tf and Fa in Water

In the Tf-W medium at v% of Tf > 10 conductometry, calorimetry and tensiometry produced unusual or non conventional behavior. In conductometry, 20 30 and 40 v% of Tf produced increased Λ with increasing [SDS] which was reverse of what was found at v% $\leq$ 10. The increase of Λ with [SDS] was unusual. It is known that by interionic interaction Λ decreases with increasing concentration of an electrolyte in a medium, without much interaction it should remain unaltered or constant as normally found in dilute solution. The observed perceptible increase in Λ was apparently abnormal. The increase in Λ in higher v% of Tf can be explained as follows. Tf is known to form hydrate with water at low temperature and high pressure (hydrate dissociation temperature at 10 w% Tf is 276.4K).[51-53] It was reported that SDS could combine with the Tf hydrate (Tf-H) to form (Tf-H-DS) with all probability by ion-dipole interaction. We presume that at 303K, solid hydrate formation was not possible but soluble solvated species of Tf-W were present in the solution which also formed Tf-W-

DS species. At higher [Tf] and appreciable [SDS], the Tf-W-DS entities got arranged under the applied electric field between two electrodes of the conductivity cell and the DS^- was transferred from one complex to the other by the "hopping" mechanism to result increasing conductance and hence increased in Λ with increasing [SDS] in solution according to the scheme 1 below.



Scheme 1. Field Induced Hopping Scheme of DS^- Transfer

At much higher concentration of Tf (≥ 50 v%) in the fairly low polar medium ion-association between Na^+ and DS^- (formation of ion-pair, triple-ion, ion-quadruple, etc.) occurred with the formation of conductance minimum followed by hyperbolic dependence of Λ on $C^{1/2}$, (described in Figure 4).

It was observed that at Tf v% 50-70 (Figure 4A) conductance minima were observed which suggested ion-association forming triple-ions at lower dielectric constant of the medium (ε= 30.62-27.13, cf. column 2 Table S1). Such a possibility was absent in Fa-W medium where ε increased with increasing concentration of Fa in the medium (cf. Table S1, column 3). Similar observations were also reported in Dn-W and Ml-W media; the former produced triple-ion at higher v% (80-88 v%) whereas the latter did not.[12] At higher v% of Tf i.e. at 80 and 90 % (Figure 4B), instead of a minimum hyperbolic dependence of Λ on $[SDS]^{1/2}$ was found. This onward hyperbolic decline suggested formation of ion-quadruples in the system. The ion-association leading to triple-ions and ion-quadruples are depicted in the scheme-below. In high dielectric medium NaDS (or SDS) completely dissociates as shown below.

$$NaDS \rightarrow Na^+ + DS^- \quad (1)$$

With lowering of dielectric constant (ε) or medium polarity leads to ion-pair formation with decrease in equivalent conductance.

$Na^+ + DS^- = Na^+DS^-$ (Ion-pair) (2)

At low ε, formation of triple ion occurs which leads to the increase in Λ, after a minimum.

$Na^+ + DS^- + Na^+ = Na^+DS^-Na^+$ or $DS^-Na^+DS^-$ (Triple-ion) (3)

Further lowing of ε forms ion-quadruple which cause removal of the minimum in the plot with the formation of a hyperbolic course in the Λ vs $C^{1/2}$ plot.

$Na^+ + DS^- + Na^+ + DS^- = Na^+DS^-Na^+DS^-$ or $DS^-Na^+DS^-Na^+$ (Ion-quadruple) (4)

Using Fuoss-Kraus rationale[54,55] we had calculated the ion-pair and triple-ion formation constants for SDS micellization in Dn-W medium,[12] which did not work in the present system of Tf-W (the results were not consistent with expectation). Tf-W medium was different from Dn-W in this respect. Computation procedure failed to quantify the observation. We could not reason it out.

Calorimetric thermograms became unusual also beyond 10 v% of Tf, formation of micelle was not detected. From 20-35 v% abnormality the thermogram pattern was visible. From 40-70v% the thermograms produced initial breaks at 4.79 mM and a minimum at 22.1 mM (in this trend ΔH-[SDS] plot at 70 v% reached nearly to zero at its minimum; the 80 and 90 v% courses emerged into the negative enthalpy zone). The above phenomena we consider were the consequence of ion-association (ion-pair, triple-ion and ion-quadruple formation) of SDS with decreasing polarity of the medium. In Figure 2 A(II) each thermogram evidenced two inflections (crest and trough). There difference was taken as the enthalpy of ion-association (ΔH_{IA}). For a clear display the thermogram for 90 v% Tf was chosen on which the two inflection points are marked as I_a and I_b. The height between the two was the corresponding ΔH_{IA} in 90 v% Tf as labeled in the diagram. The results obtained following this procedure are presented in Table 3. From the thermometric behavior at different v% of Tf, we considered the 10-35 v% zone as the “dead zone” of the mixed solvent system. Such a “dead zone” for the SDS-Dn-W system in the v% region of 50-75 was reported by us.[12] Dead zones in the mixed solvents of Dn and W was also reported by Hollamby et al.[19]

It was observed that conductometry failed to detect CMC in Fa-W medium beyond 70 v% (Figure 1B, inset). The conductometry plots for 70 and 80 v% of Fa were nearly linear with negative slopes. Calorimetry results were nicely CMC forming exothermic events up to 70 v% of Fa. The thermogram patterns at 80, 90 and 100 v% were different producing tendencies of endothermic up turns at [SDS] ≈ 110 mM. Experimental limitations restricted to take measurements at higher [SDS] required following the dilution protocol. It was observed in tensiometry that SDS formed self-association even in pure Fa (footnote c, Table 1): in Figure 3B, results up to 100 v% are presented. Amphiphile aggregation in pure Fa was also reported in the past.[29,30,34,36] The calorimetric and conductance results were based on changes in the bulk behavior of SDS, they did not affect the interfacial properties, and hence the tensiometric profiles were not abnormal (some sorts of aggregate formation was possible). NMR diffusion also corroborated self-aggregation at 67.8 mM at 60 v% of Fa. At higher concentration (100 v%) the diffusion course declined without a break as the [SDS] studied up to 100 mM which was considerably lower than the CMC (208 mM) type registered in tensiometry.

Additional support to the possible formation of CMC was tested by viscosity measurements. Two graphical presentations (Figure S3) are shown where micelle formation at 10 v% of Tf was revealed which at 30 and 70 v% were absent (ion-association at 70 % was supported from conductance and calorimetric measurements; viscosity would not be that sensitive to detect ion association phenomenon). Micelle type aggregation at 50 and 70 v% of

Fa in the Fa-W medium was unambiguously evidenced from viscometry. Association of SDS in pure Fa also supported from viscosity measurement.

3.4 Microstructures of SDS in Tf-W and Fa-W media

3.4.1 NMR study: Determination of diffusion coefficient by NMR of SDS in D_2O, Tf-D_2O and Fa-D_2O media also revealed aggregation of SDS in support of the findings from other methods (representative illustrations are shown in Figure 5 (A, B)), and results are presented in Table 4. The maximum concentration of Tf and Fa studied by NMR were 70 and 95 v%, respectively. An inflection for assembly formation was observed in 70 v% Tf-W medium but such inflections were not obtained at 80 and 95 v% of Fa in D_2O due to the limitations of using higher [SDS] in the experimental protocol (Figure 5B). ^{23}Na relaxation (T_1) dependence on [SDS] in Tf/D_2O mixed system also supported micellization at 5 and 10 v% of Tf but not at higher v% (Figure S4).

The study of ^{13}C chemical shifts of SDS alkyl chain carbons provided a qualitative perception of the interaction sites of both Tf and Fa for SDS. The results for the mixed solvent systems are depicted in Figure 5C and D. For both Tf and Fa, the C_1 carbon of SDS experienced a significant upfield shift which is appreciably more for Tf than Fa. Thus, both Tf and Fa became associated with SDS near its head group region[56] more strongly by Tf than Fa; a phenomenon comparable with that of alcohols[57] and pluronics (triblock co-polymers)[58,59] reported earlier. Increasing concentration of the organic solvents enhanced the extent of the upfield chemical shift of C_1 carbon suggesting increased localization of both Tf and Fa with SDS close to its head groups. For Tf, C_2 and C_3 carbons evidenced notable downfield shifts which did not the other carbons C_4-C_{11} (Figure 5C). The terminal C_{12} experienced marginal upfield chemical shift; conformation change of C_{12} towards gauche was envisaged. The downfield shift for C_2 and C_3 suggested that the added solvents penetrated into the interior of the SDS micelles up to C_3. On the other hand for Fa besides C_2 and C_3

downfield shifts were also found for all the carbons; marginal from C_4 to C_{11} but prominent for C_{12}. In the first place Fa (Figure 5D) also penetrated up to C_3 carbon in the SDS micelles; interaction was much lower from C_4 to C_{11} but more prominent at C_{12} in 60 and 80 v% of Fa. A conformational transition to trans occurred.

It should be mentioned that in the Tf-W medium beyond 10 v% of Tf, SDS did not form micelle (Table 1), the solvent molecules were freely interacting with the amphiphiles. The local environment polarity, viscosity, etc influenced the conformation change of C_{12} and the observed upfield shift was the average of these influences. Similarly, in Fa-W medium at higher concentration, 70 v% and above, for measurement restrictions the [SDS] used was below CMC, and hence the non micellized amphilhiles freely interacted with the solvent; the environmental factors led the conformation more towards trans causing fair downfield chemical shifts for C_{12}.

3.4.2 SANS study: Quantitative estimation of aggregate morphology, $\bar{n}$ and micelle charge were obtained from model fitting of the SANS spectra. Micro-aggregates of SDS were modeled as charged prolate ellipsoids interacting through a screened coulomb potential.[60] SANS data were analyzed using this model wherein the differential scattering cross section per unit volume (dΣ /dΩ) as a function of scattering vector ‘q’ can be written as

$$\frac{d\Sigma}{d\Omega} = n_d(\rho_m - \rho_s)^2 V^2[< F(q)^2 > + < F(q) >^2 \ (S(q) - 1)] + B \tag{5}$$

where n_d denotes the number density of micelles, ρ_m and ρ_s are the scattering length densities of the micelle and the solvent respectively, and V is the micelle volume; F(q) is the single particle form factor, and S(q) is the inter-particle structure factor. B is a constant term which represents the incoherent scattering background coming mainly from the hydrogen atoms present in the sample. F(q) is calculated using the relations:

$$F(q,\mu) = \frac{3(\sin x - x\cos x)}{x^3} \qquad (6)$$

$$x = q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2} \qquad (7)$$

where 'a' and 'b' are the semimajor and semiminor axis of an ellipsoid micelle ($a > b = c$), respectively, and μ is the cosine of the angle between the directions of 'a' and the wave vector 'q'. The inter particle structure factor S(q) was calculated using the expressions derived by Hayter and Penfold from the Ornstein-Zernike equation making the rescaled mean spherical approximation (RMSA).[61] The fractional charges of the semimajor and semiminor axes are used as the variables in the fit. For a better fit, a polydispersity in the semimajor axis was necessary, and was done using the Schultz distribution;[62] a polydispersity of about 0.2 was used in the process. Average micelle aggregation number was calculated from the relation, $\bar{n} = 4\pi ba^2/v$ where v is the surfactant monomer volume (found from Tanford formula[63]). It was found that the experimental data were found to fit well up to 10 v% and 70 v% of Tf and Fa, respectively. The values of the fitted parameters namely, semi-major axis (a), semi-minor axis (b), aggregation number ($\bar{n}$), and fractional charge (α) on the micelles are presented in Table 5 (section A). The prolate ellipsoid micelle model was found to be inadequate at higher v% of the nonaqueous solvents (> 10 and 70 v% for Tf and Fa, respectively). This was due to the complexity of calculation of S(q) where the charged head groups of SDS remained hidden by solvation.[64] The mean aggregation number was, therefore attempted to calculate from the maximum peak position(Q_{max}), assuming a simple cubic (SC) or face-centered cubic (FCC) packing of the micelles proposed by Chen et al,[65] in which the inter-particle distance D between the micelles is given by

$$D = 1/\sqrt{2}(4000\bar{n}/N_A C)^{1/3} 10^8 \overset{0}{\mathrm{A}} \qquad (8)$$

where N_A is the Avogadro number. Assuming face-centered cubic (FCC) geometry, the peak position (Q_{max}) can be related to the inter-particle distance D as,

$$Q_{max} D = \sqrt{6}\pi = 7.695 \qquad (9)$$

Thus,D and hence $\bar{n}$ can be obtained from the peak position (Q_{max}).

Assuming simple cubic (SC) micelles, the aggregation number is related to Q_{max} by the relation,[66]

$$Q_{max} = 2\{4^{1/3}\pi(N_A C/4000\bar{n})^{1/3}\}\, X\, 10^{-8}\ \overset{0}{A}^{-1} \qquad (10)$$

Wu et al.[67] have proposed an empirical formula based on the fitting of their data to several samples connecting D and Qmax. Thus,

$$Q_{max} D = 6.8559 + 0.0094D \qquad (11)$$

The aggregation number ($\bar{n}$) can be calculated by using equation (8) and (11).

Such values are summarized in Table 5 (section B). Among the three sets FCC and Empirical model values were close than the SC model. Thus, FCC model based values were acceptable. But the FCC based results were found up to 60 v% of Tf and 100 v% of Fa. In Tf-W medium after 60 v% SANS spectra indicated a new phenomenon; the lower ‘q’ region increased suggesting enhancement of intermolecular interaction. Hollamby et al.[19] had proposed that the estimated $\bar{n}$ values < 20 are not reliable with a model other than globular or spherical having non-defined monomer agreegation. In that respect results for Tf-W ≥ 20 v% and Fa-W ≥ 70 v% were not FCC either; they might be undefined small aggregates or “RAGA” (randomly arranged globular assembly) proposed by us.[12] Hollamby et al.[19] reported $\bar{n} = 8$ for AOT in 1:3 (Dn:D_2O) medium which declined with increasing proportion of Dn in D_2O. In cyclohexane “Hank-like” micelles[68,69] of pentaethylene glycol monodecyl ether ($C_{12}E_5$) at 2.5 w% with aggregation number of 5 was also observed.

3.5 Correlation of ΔG_m^0 with solvent parameters

Effects of mixed solvents on the self-assembly formation of surfactants are reported in literature.[10-25] In most cases, attempts were made to correlate CMC with solvent parameters viz., viscosity(η_o), permittivity(ε), dipole moment(μ), $E_T(30)$, Gordon parameter(G), Hansen-Hildebrand parameters (dispersion, δ_D; polar, δ_P; hydrogen bonding, δ_h), polarity index (π^*), and Gutman donor number (DN), etc. Hydrogen bonding, solvent structure, solvent polarity and viscosity (or fluidity) can affect the molecular association of the amphiphile species, a single parameter may not be adequate for the explanation. Further, instead of CMC, ΔG_m^0 is considered a better parameter for the above correlation, particularly for ionic micelles that distinctly bind counter-ions. For an exact thermodynamic comparison, the activity derived ΔG_m^0 values should be used which was not done in the past. In a previous study,[12] we had used activity derived free energy values for such a correlation. The same rationale was herein used; the solvent parameters considered were ε, E_T (30), G, and η_0. The results are presented in Figure S5. The ΔG_m^0 vs ε^{-1} plots for Tf-W and Fa-W media evidenced reverse dependence reflecting the decrease and increase in ε of Tf-W and Fa-W media, respectively with increasing concentration of the non aqueous solvent in them. All the other parameters produced identical trends for both the solvent pairs. The plots were mostly curved, except Tf-W system correlated with G (which showed linearity). In the existing literature, a single linear correlation between ΔG_m^0 (concentration derived) and G for different surfactant-mixed solvent systems can be found,[16] which was oversimplification as noted earlier.[12] Here we found linearity in Tf-W solvent medium but not in Fa-W medium. Non linear correlation for micellization of SDS in Dn-W and Ml-W media was observed by us.[12] Of all the solvent parameters herein used, G is essentially related with the interfacial tension, γ ($G = \gamma/\overline{V}_m^{1/3}$, $\overline{V}_m$ is the molar volume of the mixed solvent). The other parameters ε, E_T (30), and η_0 relate to bulk properties. Therefore, ΔG_m^0 (a bulk property as well) is more relevant to correlate with ε, E_T (30), and η_0 than G in different aquo-organic solvent systems. Thus, literature reports on linear correlation of CMC and apparent free energy of micellization with G for different aquo-organic solvent systems were not based on strong grounds, and perhaps fortuitous. Since breaking of hydrogen bond of water has a direct say on amphiphile self-association (urea effect), Hansen-Hildebrand hydrogen bonding parameter (δ_h)[70] could be a better correlator for ΔG_m^0. This is presented in Figure 7. Since δ_h values are not available for mixed solvents, those were found from the following reciprocal relation,[12] $(\delta_h)_{mix} = (\sum X_i / \delta_{hi})^{-1}$, where X_i and δ_{hi} are the mole fraction and Hansen-Hildebrand solubility parameter of the ith species in solution, respectively. It was found that the results of Tf-W and Fa-W mixed systems closely correlated with the ΔG_m^0 following nearly the same curvilinear course. Hence hydrogen bonding primarily influenced the self-aggregation of SDS in the studied mixed solvent media. Similar was the finding on SDS micellization in the mixed media of Dn-W and Ml-W[12] (also shown in the Figure 7).

4. Conclusion

Amphiphile aggregation in aqueous medium is fairly controlled by the hydrogen bonding among the water molecules along with the polar, nonpolar and electrostatic effects coming from the amphiphile type and class. Temperature, pressure and additive can also influence the self-aggregation. In nonaqueous media nonperturbed solvent structure may not lead to aggregation, and micellization in particular.[2,3] Strong dipolar interactions among the amphiphile molecules produce large aggregates otherwise they are small. In mixed aquo-organic media addition of small proportion of the nonaqueous solvent (co-solvent) may enhance the amphiphile self-aggregation by solvophobic effect which with large proportion retards the process by solvophilic effect.

The moderately polar aprotic Tf decreased the CMC of SDS up to 6 v% by solvophobicity, the micelle aggregation number also decreased. Above 10 v%, micelle formation was not observed. From 10 to 40 v%, Λ vs $C^{1/2}$ plots increased without breaks for CMC. The ion-dipole interacted complex between solvated Tf (or Tf-W) and DS^- i.e., Tf-W-DS) under the applied electric field transferred DS^- by hopping mechanism (Scheme 1), a conductance percolation-like phenomenon "found in W/O microemulsion"[71] occurred. Beyond 40 v%, decreasing Λ forming minimum, and thereafter disappearance of the minimum forming a rectangular hyperbolic pattern in the Λ vs $C^{1/2}$ plots were found (in the range between 50-90 v%) like what was observed for SDS in Dn-W medium at higher v% of Dn.[12] The formation of ion-pair, triple-ion and ion-quadruple were suggested in the system with decreasing ε (30.62-9.84). Inflections in NMR diffusion at 70 v%, and in ITC at 70, 80 and 90 v% supported the ion-association process like that observed in Dn-W medium. Above 10 v% of Tf, SANS analysis based on FCC model supported small assemblies up to ~60v% (those may be the Tf-W-DS aggregates (as proposed in scheme 1). A "randomly arranged globular assembly" (RAGA) proposed for SDS aggregates in Ml-W medium[12] was considered valid in Fa-W medium ≥ 80 v%. The upturn in the ITC thermogram (Figure 2B(II) inset) at 100 v% of Fa was at 110 mM; the NMR diffusion in 95 v% of Fa could not be measured beyond 100 mM of SDS for experimental limitations (Figure 5B) so an inflection for its self-association of amphiphile was not observed. SANS experiments (Figure 6B) found a broad peak with lower intensity. Results fitted with prolate ellipsoid micellar model up to 70 v% with a fairly large $\bar{n}$ whose semi-major axis decreased with increasing fractional charge. Based on FCC model, at higher v%, $\bar{n} < 20$ was not reliable; globular micelle model was enviseged.[19] We recently proposed a "randomly arranged globular assembly" (RAGA) for SDS in high v% of Ml in water. Similar assemblies were also considered in Fa-W medium at v% >70.

The correlations of ΔG^{o}_{m} with different solvent parameters ε, $E_T(30)$, G, and η_0 (Figure S5) were curvilinear excepting G for Tf-W medium. Anticipating hydrogen bonding has a major role in micelle formation, correlation of ΔG^{o}_{m} with the Hansen-Hildebrand hydrogen bonding parameter (δ_h) was tested (Figure 7). For both the mixed Tf-W and Fa-W, ΔG^{o}_{m}-δ_h patterns were closely related. Similar was the correlations in Dn-W and Ml-W mixed media studied earlier[12] (results displayed in Figure 7). Thus hydrogen bonding in the mixed solvents has a major say on the amphiphile self-assembly formation. More studies in this direction are warranted.

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Table 1: CMC and β for SDS Determined in Mixed-Solvent Media by Different Methods at Varied Concentrations of Tetrahydrofuran (Tf) and Formamide (Fa) in Water at 303 K[a,b,c]

Solvent composition v%(X_{Tf}, X_{Fa})	CMC (Tf-W)			CMC (Fa-W)			CMC_{ave}	β
	Cond	Cal	ST	Cond	Cal	ST	Tf-W (Fa-W)	Tf-W (Fa-W)
0(0 , 0)	8.5	8.6	8.7	8.5	8.6	8.7	8.6	0.60
1(0.002,0.005)	6.8	7.1	7.2	6.9	6.3	6.7	7.0 (6.6)	0.49 (0.48)
2(0.005,0.009)	6.1	6.3	6.2		7.5	7.2	6.2 (7.3)	0.37 (0.49)
3(0.007,0.014)				7.9	7.1	7.6	(7.5)	(0.52)
4(0.009,0.018)	5.1	5.0					5.0 ( )	0.22 ( )
6(0.014,0.028)	4.8	4.6	4.7				4.7 ( )	0.24 ( )
10(0.024,0.048)	6.9	6.1	6.5	10	12	11	6.5 (11)	0.12 (0.43)
20(0.053,0.102)				14	15	17	(15)	(0.26)
30(0.087,0.163)				22	24	25	(24)	(0.24)
40(0.129,0.233)				37	37	40	(38)	(0.19)
50(0.183,0.312)				54	57	55	(55)	(0.16)
60(0.251, 0.406)				74	74	71	(73)	(0.13)
70(0.343, 0.515)				112	132	119	(121)	(0.11)

[a,] CMC is expressed as a millimolar concentration and the standard deviations (SD) for the CMC are ±3, ±2, and ±4% for conductometric (cond), microcalorimetric (cal), and tensiometric (ST) methods, respectively.

[b,] Parameter β was obtained from the relation $\beta = 1 - (S_2/S_1)$,[12] where S_1 and S_2 are the premicellar and postmicellar slopes of the linear conductance vs concentration plots.

[c,] CMC value of SDS in Fa at 303 K temperature by tensiometry is 208 mM.

Table 2: $\Gamma_{\max}, A_{\min}, \Delta G^0_m, \Delta G^0_{ad}, \Delta H^0_m$ and ΔS^0_m for SDS Self-Aggregation in Mixed Media of Tf-W, and Fa-W at 303 K[a, b, c]

Solvent composition (v%)	$10^6\Gamma_{\max}$		$A_{\min}$		$-\Delta G^0_m$		$-\Delta G^0_{ad}$		$-\Delta H^0_m$		ΔS^0_m	
	Tf-W	Fa-W	Tf-W	Fa-W	Tf-W	Fa-W	Tf-W	Fa-W	Tf-W	Fa-W	Tf-W	Fa-W
0	2.63	2.63	0.63	0.63	36.2	36.2	53.1	53.1	2.43	2.43	111.5	111.5
1	1.79	2.15	0.92	0.77	34.4	34.4	51.4	50.9	2.52	3.90	105.2	100.6
2	1.59	1.93	1.04	0.86	32.1	34.7	48.9	49.2	2.64		97.2	
3		1.84		0.90		34.9		48.6		5.76		96.2
4					30.1				3.27		88.6	
6	1.16		1.43		29.3		46.9		5.20		79.5	
10	0.93	1.76	1.79	0.94	27.8	31.8	40.2	47.9	6.67	6.40	66.4	83.8
20		1.57		1.06		27.5		45.7		9.87		58.2
30		1.45		1.15		26.0		44.1		10.3		52.2
40		1.38		1.20		24.3		42.9		7.21		56.4
50		1.27		1.31		23.4		41.4		6.88		54.5
60		1.19		1.39		23.0		39.5		6.67		53.9
70		1.11		1.49		22.8		38.7		6.58		53.5

[a] $\Gamma_{\max}$, $A_{\min}$, ΔG^0_m, ΔG^0_{ad}, ΔH^0_m, and ΔS^0_m are expressed in mol m^{-2}, nm^2 molecule^{-1}, kJ mol^{-1}, kJ mol^{-1} , kJ mol^{-1} and J mol^{-1} K^{-1}, respectively.

[b] The relations used for calculation of different parameters are,

$$\Gamma_{\max} = -\frac{1}{2.303iRT} \lim_{a_{SDS}\to cmc} \frac{d\gamma}{d\log a_{SDS}} \quad \text{where, } a_{SDS} = X_{SDS} f'_{\pm} \text{ and}$$

$$A_{\min} = \frac{10^{18}}{N_A\,\Gamma_{\max}}\,;\ \Delta G^0_{ad} = \Delta G^0_m - \frac{\pi_{CMC}}{\Gamma_{\max}}$$

Here, $\Gamma_{\max}$, $A_{\min}$, ΔG^0_{ad} and i are the Gibbs surface excess at the air/ solution interface, the minimum area covered by the amphiphile head group, Gibbs free energy of adsorption and number of species formed per SDS monomer in solution. N_A, R and T are Avogadro number, universal gas constant and experimental temperature (303 K), respectively. π_{CMC} = surface pressure of amphiphile at the air/solution interface at CMC ($\gamma_{solvent}$-γ_{CMC}) and i =2 in the Gibbs surface excess calculation.

[c] Thermodynamic calculations were done using activities in rational scale. The rational activity coefficient $f'_{\pm}$ required for the conversion of concentration into activity was found from the relation presented in the supporting materials.

Table 3: Enthalpy of ion-association of SDS in different Tf-W solvent composition at 303 K

Solvent Composition (v%)	ΔH_{IA} / kJ mol^{-1}
40	-10.62
50	-4.54
60	-2.41
70	-1.69
80	-1.84
90	-2.66

Table 4: Inflections of self-diffusion by NMR, enthalpy of dilution by calorimetry of SDS in Tf-W and Fa-W media[a,b]

Tf-W(A)				Fa-W(B)		
V%	**NMR**	**Calorimetry**		**V%**	**NMR**	**Calorimetry**
		Inflection I	**Inflection II**			
5	4.20	4.82	-	10	8.40	12.0
10	6.10	6.50		20	10.2	15.0
25	-	-		40	40.8	37.0
35	-	-		60	67.8	74.0
40	ND	22.1	-	80	-	-
50	ND	21.5	-	95	-	-
60	ND	19.8	-			
70	22.2	8.30	20.1			
80	ND	7.08	19.8			
90	ND	4.79	17.7			

[a], Inflections in ^{23}Na relaxation experiment for SDS in 5, 10, 70 and 95 v% Tf are 4, 4, 6 and 2, respectively.

[b], ND means that not done.

Table 5: Aggregation Parameters of SDS Micelles as Derived from the Peak Position using Different Models of Packing at 303 K

Section (A)

Solvent Composition (v%)	**Water-Tetrahydrofuran System (I)**			
	Semi-major axis	Semi-minor axis	Aggregation Number	Fractional Charge
0	36.51	16.7	77.8	0.35
10	26.40	16.7	46.5	0.45
	Water-Formamide System (II)			
0	27.29	16.7	91.0	0.30
10	21.77	16.7	72.6	0.38
30	16.31	16.7	54.4	0.57
50	12.53	16.7	41.8	0.88
70	14.39	16.7	29.7	0.94

Section (B)

Solvent Composition (v%)	Peak Position **(Q_{max} / Å^{-1})**	Aggregation Number		
		(FCC model)	(SC model)	(Empirical)
Water-Tetrahydrofuran System (I)				
0	0.07799	78	60	81
10	0.09368	46	36	45
20	0.11825	21	16	19
40	0.13380	15	11	13
60	0.14271	12	9	11
Water-Formamide System (II)				
0	0.09368	92	71	90
10	0.10039	74	57	71
30	0.11156	52	40	48
50	0.12048	38	30	35
70	0.12493	28	21	25
90	0.13383	18	14	16
100	0.13827	14	11	12

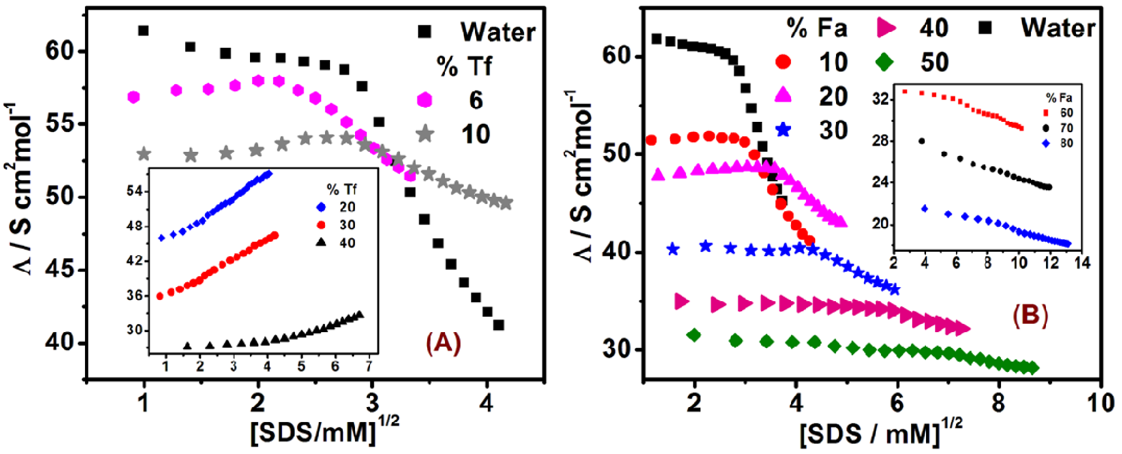

Figure 1: Conductometric profiles for SDS in Tf-W and Fa-W media at different solution compositions at 303 K. **(A):** Λ vs $[\mathrm{SDS}]^{1/2}$ plots with 0, 6 and 10 v% of Tf along with water in main plot, **(Inset):** 20, 30 and 40 v% Tf; **(B):** Λ vs $[\mathrm{SDS}]^{1/2}$ plots with 0, 10, 20, 30, 40, and 50 v% of Fa along with water in main plot, **(Inset):** 60, 70 and 80 v% Fa.

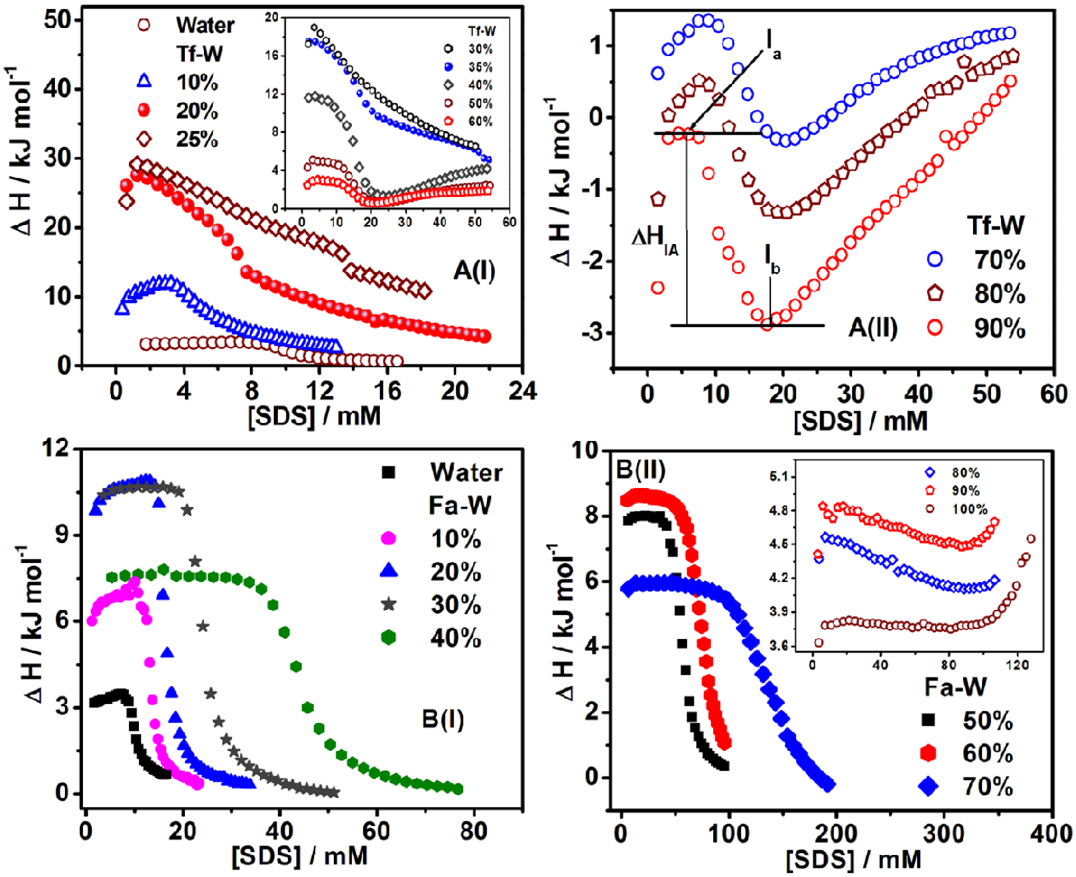

Figure 2: Calorimetric profiles of SDS in different Tf-W and Fa-W mixed solvent media at 303 K.; **A(I):** 10, 20 and 25 v% Tf along with water in main plot, **(Inset):** 30, 35, 40, 50 and 60 v% Tf and **A(II):** 70, 80 and 90 v% of Tf in main plot, **B(I):** 10, 20, 30 and 40 v% Fa along with water and **B(II):** 50, 60 and 70 v% Fa in main plot, **(Inset):** 80, 90 and 100 v% Fa.

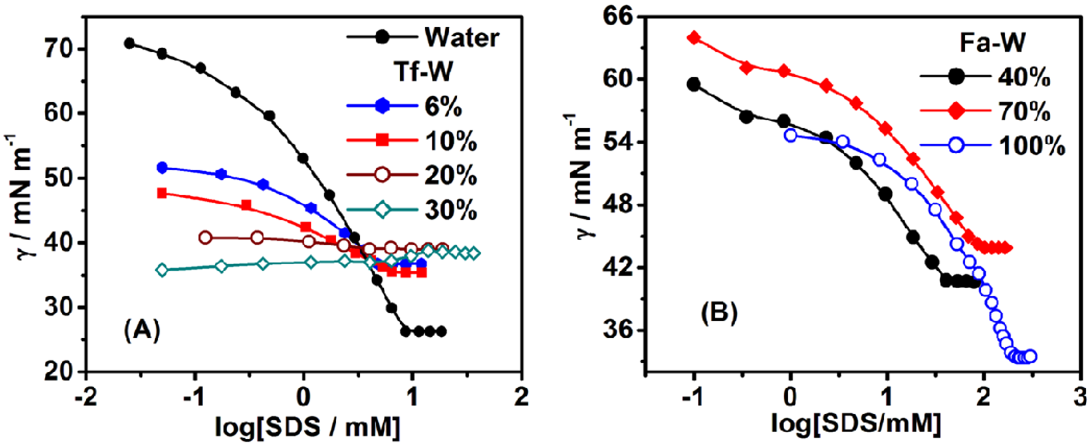

Figure 3: Plots of surface tension as a function of [SDS] in different mixed solvent media at 303 K. **(A):** 6, 10, 20 and 30 % Tf along with water, **(B):** 40, 70 and 100 v% of Fa.

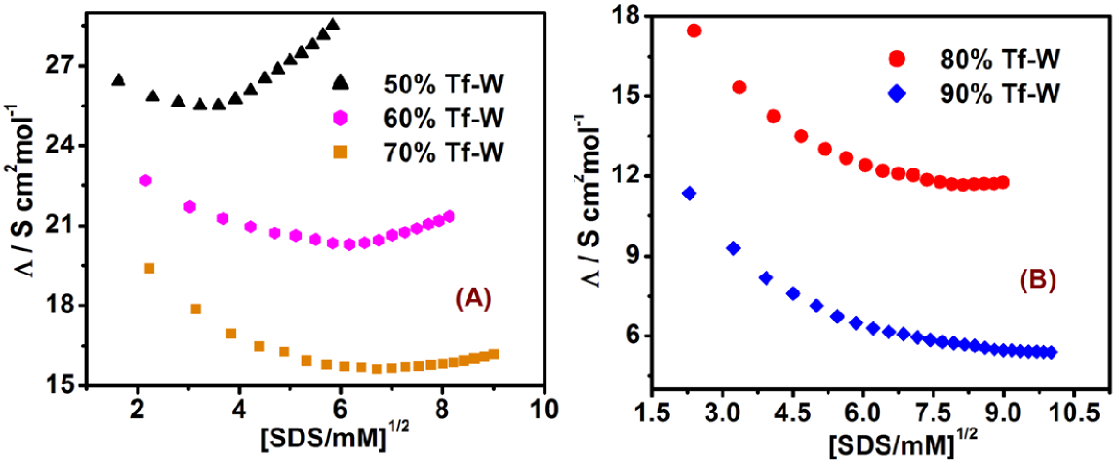

Figure 4: Λ vs $[SDS]^{1/2}$ plots in Tf-W medium at 303 K. **(A):** 50; 60 and 70 v% of Tf and **(B):** 80 and 90 v% of Tf.

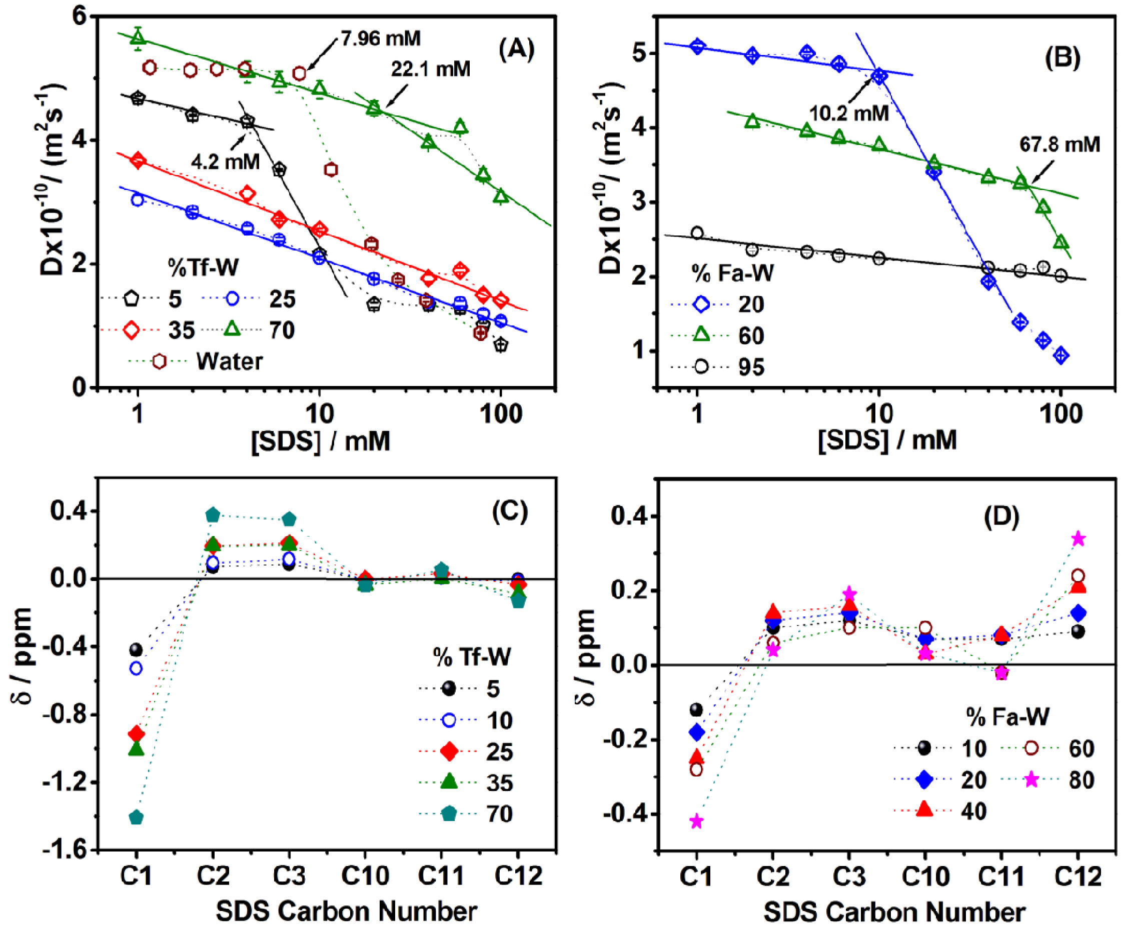

Figure 5: Self-diffusion coefficient profiles of SDS in D_2O and **(A):** Tf-D_2O; **(B):** Fa-D_2O media, and ^{13}C chemical shift (δ/ppm) vs SDS carbon number plots relative to SDS in D_2O in different mixed systems. **(C):** in different Tf-D_2O mixed proportions and **(D):** in different Fa-D_2O mixed proportions.

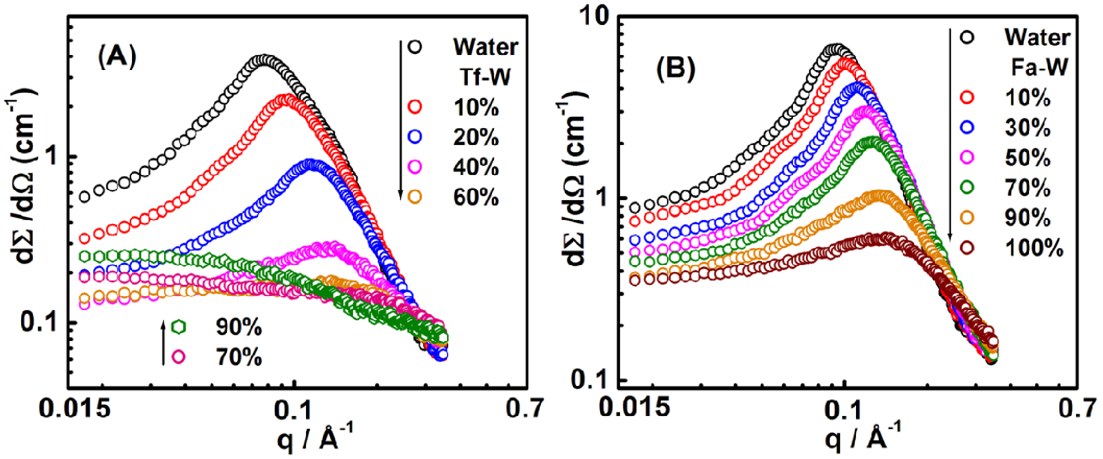

Figure 6: SANS spectra for SDS **(A):** in different composition of Tf-W mixtures along with water (0.2 M) and **(B):** in different composition of Fa-W mixtures along with water (0.4 M) at 303 K.

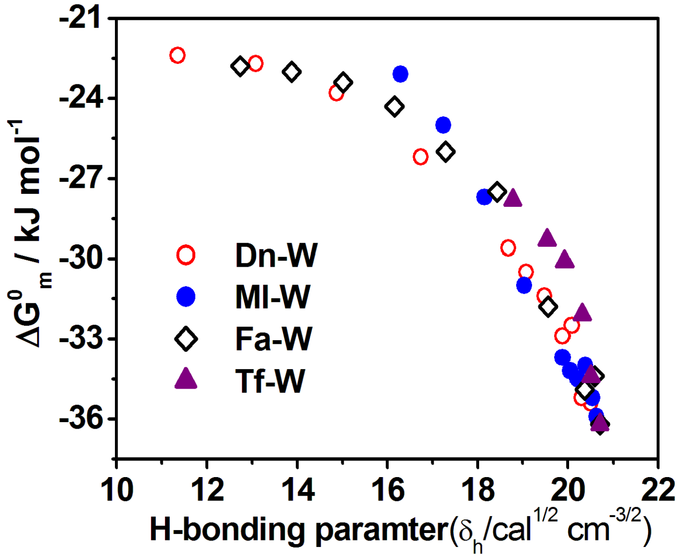

Figure 7: Free energy of micellization (ΔG^0_m) vs Handen hydrogen bonding parameter (δ_h) in different Dn-W, Ml-W, Tf-W, and Fa-W mixed solvent media at 303 K.

Graphical Abstract:

Micellization and Related Behavior of Sodium Dodecylsulfate in Mixed Binary Solvent Media of Tetrahydrofuran (Tf) and Formamide (Fa) with Water: A Detailed Physicochemical Investigation

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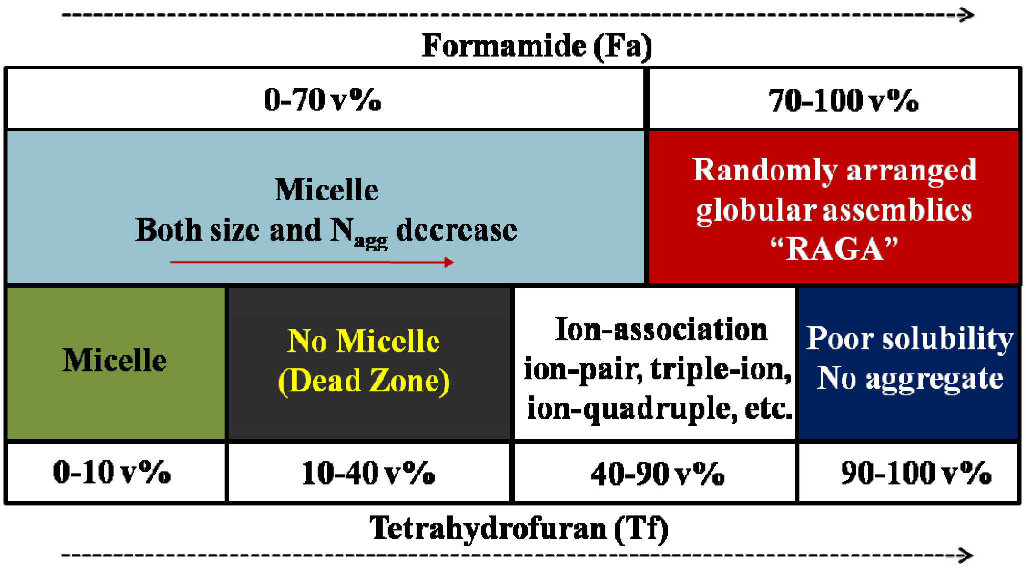

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Formamide (Fa)

0-70 v%	70-100 v%
Micelle Both size and N_{agg} decrease	Randomly arranged globular assemblies "RAGA"

Micelle	No Micelle (Dead Zone)	Ion-association ion-pair, triple-ion, ion-quadruple, etc.	Poor solubility No aggregate
0-10 v%	10-40 v%	40-90 v%	90-100 v%

Tetrahydrofuran (Tf)

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Behavior of SDS with increasing v% of Tf and Fa in water at 303K