

# Physicochemical Studies on the Interfacial and Bulk Behaviors of Sodium *N*-Dodecanoyl Sarcosinate (SDDS)

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**Abstract** Sodium *N*-dodecanoyl sarcosinate (SDDS), a novel amino-acid based surfactant, has immense biological and industrial importance. Although it is being used in a number of cosmetic formulations, systematic analysis of the bulk and interfacial properties of the surfactant is scarce in the literature. In this study, effects of salt, temperature, and pH on the self-association and related properties of SDDS have been examined in detail using methods such as tensiometry, conductometry, fluorimetry, pH-metry, spectrophotometry, calorimetry, and circular dichroism. The nature of amphiphilic packing and the aggregation numbers of the assemblies have been deciphered. Properties of the acid form of the surfactant have also been explored. The results have been conceptually rationalized and systematically presented together with associated energetics of the interfacial adsorption and self-aggregation of the surfactant in the bulk.

**Keywords** Acyl sarcosines · Micellization · Interfacial parameters · Salt effect · Cotton effect

## Abbreviations

HDSS Dodecanoyl sarcosinic acid  
MDGA *N*-methyl-*N*-decanoyl glucamide  
SDS Sodium dodecyl sulfate  
SDDS Sodium *N*-dodecanoyl sarcosinate

## Introduction

A group of novel amino-acid based surfactants are gaining importance both industrially and academically [1–7]. They are reported to be superior to conventional surfactants in several aspects, they are mild, less irritating to the skin, easily biodegradable, have better stability towards hard water, and many of them possess antimicrobial activities [8]. These are the salts of long chain *N*-acyl amino acids, generally, behaving as anionic surface active agents having the long chain acyl radical as the lipophilic group and the carboxylic acid as the hydrophilic head group. The *N*-acyl derivatives of *N*-methyl glycine, generally referred to as the acyl sarcosines, are considered modified fatty acids with greater solubility and increased acidity of the carboxylic acid group compared to the parent fatty acid. A synonym for lauroyl sarcosine is *N*-methyl-*N*-(1-oxododecyl) glycine, it is a modified lauric acid in which the hydrocarbon chain is interrupted by an amidomethyl (–CONCH<sub>3</sub>–) group in the alpha position. The sodium salt of lauroyl sarcosine is available commercially as a colorless to slightly yellow liquid, as a 30% aqueous solution, as solid flakes, or as a substantially anhydrous white powder with 97% active content.

They are used in a large number of cosmetic formulations [9–12] as hair-conditioning agents and surface-cleansing agents. In soaps, high concentrations up to 12.9% of sarcosinates are reported to be present [8]. They are non-irritating and non-sensitizing to animal and human skin, although they can enhance the penetration of other ingredients through the skin. Because sarcosine can be nitrosated to form *N*-nitrososarcosine, a known animal carcinogen, these ingredients should not be used in cosmetic products in which *N*-nitroso compounds may be formed. Thus, it may be suggested, that these acyl sarcosines and sarcosinates are

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safely used as rinse-off products. They may be formulated safely in leave-on products at concentrations up to 5%, the highest concentration tested in clinical irritation and sensitization studies.

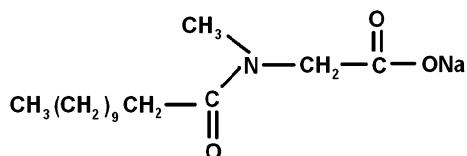
Although sarcosines and sarcosinates have immense biological and industrial importance, studies regarding their solution properties are quite rare in the literature. Spivack [7] has extensively reviewed several synthetic routes and surfactant-based applications of *N*-acylamino acid salts. Several other workers have studied surfactant properties of different *N*-acylamino acid salts in solution [1, 5, 6]. A detailed report on the properties, reactivity, synthesis, and usage of several such surfactants have been presented in the International Journal of Toxicology, 2001 [8].

The solution and interfacial properties of sarcosinates have not been adequately studied. In view of their cosmetic and pharmaceutical uses such information is essential for their profitable applications and uses in practice. In the present study we have endeavored to investigate critically the interfacial and bulk properties of a member of this class of surfactants, Sodium *N*-dodecanoyl sarcosinate (SDDS). The self-aggregation behavior of this surfactant has been studied in salt environments, at different temperatures and pH. In addition, the acidity constant of the corresponding acid has been evaluated along with the conformational property of the salt in an aqueous medium. Such a detailed investigation on SDDS has not been done in the past. The surfactant exhibited a mild effect with regard to temperature and pH, but moderate effect with regard to salt. Increasing concentration has increased its micellar aggregation number which was again mild with salt variation. Like the *N*-methyl-*N*-decanoyl glucamide (MDGA), SDDS has shown the Cotton effect in its CD spectra due to the  $\pi$ - $\pi^*$  transition in the carbonyl group following self-association of its molecules in the form of micelles. The compound has been schematically presented in Fig. 1.

## Experimental Procedures

### Materials

The surfactant was purchased from Fluka, Germany and was used as obtained. The salts NaCl, NaI, and NaN<sub>3</sub> were



**Fig. 1** Schematic representation of the structure of the amino acid-based surfactant sodium dodecanoyl sarcosinate (SDDS)

from Merck (Germany), while NaBr was obtained from Loba Chemicals (India). LiCl, KCl, and CsCl were all purchased from Merck (Germany).

## Methods

### Tensiometry

A calibrated Krüss (Germany) tensiometer, based on the du Noüy ring detachment method, was used to measure the surface tension ( $\gamma$ ) at the air/solution interface of the surfactant solutions. Concentrated solution of a surfactant was progressively added in steps with the help of a Hamilton microsyringe in water (taken in a container) maintained at a constant temperature with an accuracy of  $\pm 0.1$  K. The surface tensions were measured allowing  $\sim 20$  min time for equilibration after each addition. The experiments were duplicated to check reproducibility and the mean values were used for data acquisition and treatment. The  $\gamma$  values were accurate within  $\pm 0.1$  mN m<sup>-1</sup>.

### Conductometry

The specific conductances of surfactant solutions were measured using a Jenway conductance bridge (UK) combined with a cell of unit cell constant. The concentration of the surfactant solution was increased progressively following the same protocol as in tensiometry. Measurements were taken after thorough mixing and allowing time for temperature equilibration. The experiments were duplicated and mean values of the results were reported and used. The uncertainties in the measurements were within  $\pm 2\%$ .

### Spectrophotometry

Absorbance measurements were taken in a UV 1601 Shimadzu (Japan) spectrophotometer using 10-mm path length quartz cuvettes. The spectra of 2  $\mu$ M pyrene solution in the surfactant solutions of varied strength were recorded in the 200–400 nm wavelength range. The concentration of the surfactant solution was varied from below to above the critical micelle concentration (CMC) by progressive addition of a concentrated solution into water with a Hamilton microsyringe. The absorbances of the main peaks in the spectra were plotted against the surfactant concentration, and the CMCs were obtained from the crossings of the straight lines depicted in the figures.

### Fluorimetry

Fluorescence measurements using pyrene as the fluorescent probe were taken using a Perkin Elmer fluorimeter LS 55

(USA) using a 10-mm path length quartz cuvette. Excitation was done at 332 nm and emission was recorded in the 340–450 nm ranges. The slit widths for both excitation and emission were fixed at 12 nm. Surfactant solutions were taken 10 times their CMCs, and pyrene concentration in solution was kept at around 2  $\mu\text{M}$ . To determine the aggregation number, the quencher (CPC) was added progressively (quencher concentration was varied between 0.01 and 0.3  $\text{mM dm}^{-3}$ ) into the surfactant solution containing pyrene with the help of a Hamilton microsyringe and the fluorescence spectra were recorded.

### Calorimetry

An Omega ITC microcalorimeter of Microcal, Northampton (USA) was used for thermometric measurements. The concentrated degassed surfactant solution ( $\sim 20$  times its CMC) was taken in the micro syringe and added in steps to 1.325 mL degassed water taken in the calorimeter cell under constant stirring (300 rpm) condition. The calorimeter was set at five degrees below the required temperature with a Neslab RTE 100 bath and scanned to the studied temperature which fluctuated within the limit of  $\pm 0.01$  K. The heat released or absorbed at each step of dilution of the surfactant solution was recorded in the instrument, and the enthalpy change per mole of injectant was calculated by the ITC software. Each run was duplicated to check reproducibility.

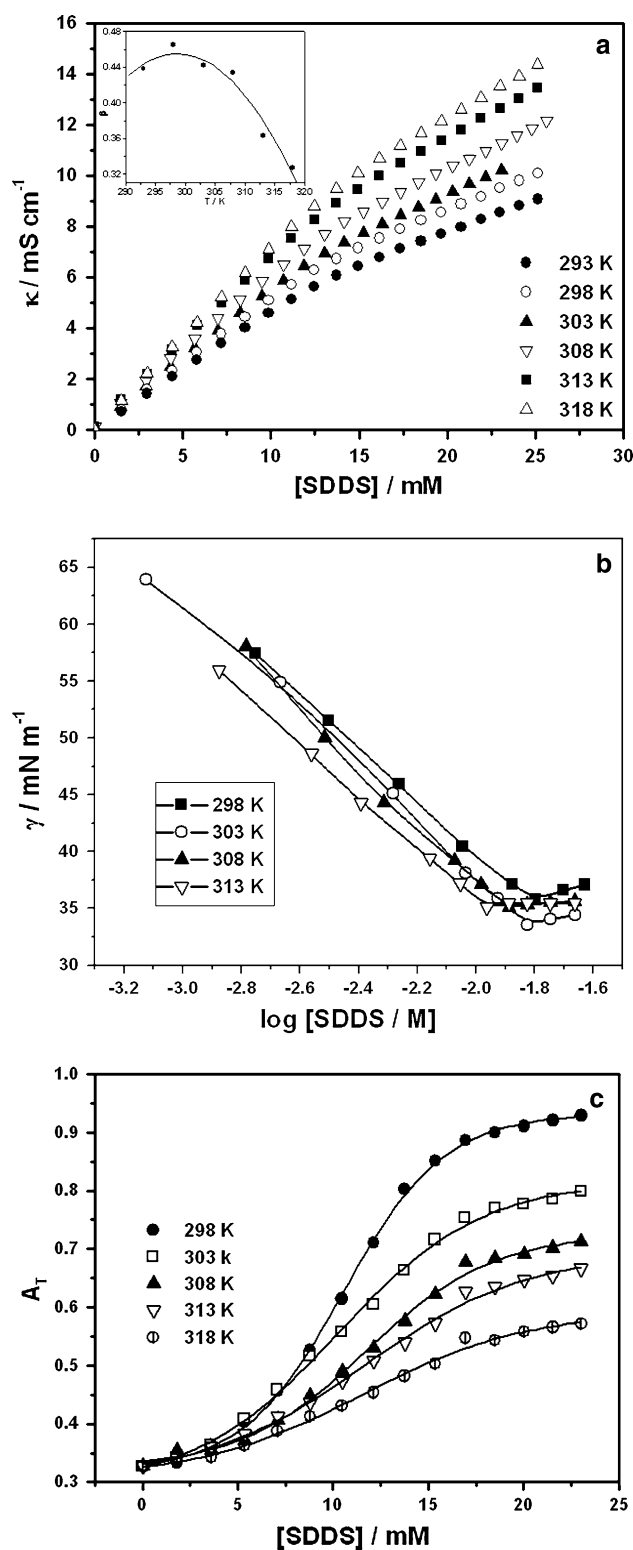
### Circular Dichroism (CD)

Far-UV circular dichroism experiments were performed using a Jasco, J-600 recording spectropolarimeter (Japan) attached to a chiller to control the temperature of the Xe-lamp and the electronic circuit. The instrument was calibrated with an aqueous solution of  $d_{10}$ -camphor-sulfonic acid using a slit width of 1 nm and scan speed of 50  $\text{nm min}^{-1}$ . A 5-mM surfactant solution was initially taken in a cuvette of 0.01 dm path length for measuring the far-UV CD spectra in the range between 200 and 250 nm. A concentrated surfactant solution was then gradually added in microliters to the cuvette to vary the [surfactant] from below to much above the CMC. The reported spectra were the average of three scans.

## Results and Discussion

### CMC of Sodium Dodecanoyl Sarcosinate (SDDS)

In Fig. 2a, b, and c several representative conductance profiles, tensiometric profiles, and spectroscopic profiles of



**Fig. 2** a Specific conductance ( $\kappa$ ) vs [surfactant] profiles for SDDS at various studied temperatures. *Inset:* Counterion binding ( $\beta$ ) versus temperature profile. b Surface tension ( $\gamma$ ) vs  $\log$  [SDDS] profiles at four different temperatures. c Total absorbance ( $A_T$ ) vs. [SDDS] profiles at various studied temperatures

**Table 1** Temperature effects on CMC,  $P$ , and energetic parameters in bulk and at the interface of SDDS in aqueous medium

Temperature (K)	Cond (mM)	Tens (mM)	Abs (mM)	$\Delta G_m^0$ (kJ mol <sup>-1</sup> )	<sup>a</sup> $\Delta H_m^0$ (kJ mol <sup>-1</sup> )	$\Delta S_m^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Gamma_{\max} \times 10^6$ (mol m <sup>-2</sup> )	$A_{\min}$ (nm <sup>2</sup> mol <sup>-1</sup> )	$\Delta G_{ad}^0$ (kJ mol <sup>-1</sup> )	$P$
293	12.9	–	–	–29.3	42.27	244.3	–	–	–	–
298	12.7	14.3	10.5	–30.5	12.24(5.61)	143.4(121.2)	2.03	0.816	–47.4	0.257
303	12.6	13.2	10.2	–30.7	–16.81(2.38)	45.8(109.2)	2.12	0.783	–48.2	0.267
308	13.3	10.6	11.7	–31.0	–44.91(0.29)	–45.2(101.6)	1.86	0.891	–51.2	0.235
313	12.8	9.97	11.7	–30.1	–72.12	–134.2	1.89	0.881	–49.9	0.238
318	12.6	–	11.5	–29.6	–98.47	–216.6	–	–	–	–

<sup>a</sup> ITC results are shown in parentheses; Standard deviations in the CMC (columns 2–4) values were  $\pm 0.18$ ,  $\pm 0.16$ , and  $\pm 0.15$  for conductivity, tensiometry, and spectrophotometry, respectively

pure sarcosinate at several temperatures are illustrated. The CMC values are listed in Table 1. The CMC of SDDS has been found to mildly decrease with increasing temperature. In comparison, the spectroscopic method has produced lower CMCs than both conductometry and tensiometry. The CMC has been observed to be method dependent [13–16]. Different methods have different sensitivities for they sense different physical properties of the materials in solution. However, the trends in the CMC values on the environmental variations are normally found to be method independent. The salt effect on the CMC studied herein (discussed later) has lent support to the above.

A literature survey supports that ionic surfactants like sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC), sodium dioctyl sulfosuccinate, cetyl ethyl dimethyl ammonium bromide (CEDAB), cetyl diethanolyl methyl ammonium bromide, tetradecyl triphenyl phosphonium bromide etc... show mild minima in their CMC versus temperature profile [17–19]. However, *N*-methyl-*N*-decanoyl glucamide (MDGA) [19], a non-ionic alkylpolyglucoside and an octyl glycoside [20, 21] also have minima in the CMC—temperature plot; ethoxylated *tert*-octylphenol [22] another non-ionic surfactant, has shown a decreasing trend in CMC with increasing temperature in the studied temperature range 288–313 K. The above account tells that the effect of temperature on CMC is system dependent. In most ionic surfactants and several non-ionic surfactants, minimum in CMC—temperature profile has been the usual trend. Factors affected by the change of temperature like surfactant solubility, desolvation, changed solvent structure, etc., play important role in this respect [23, 24]. In general, for ionic surfactants, micelle formation is favored with increase in temperature in the lower range of temperature. At a higher temperature range, the formation is disfavored due to stronger repulsion between desolvated head groups. Besides, increased thermal motion may hinder the molecular association of the amphiphiles. Therefore, a minimum in CMC is expected to be observed in the variation of CMC with temperature in the range 298–308 K. For some amphiphiles, the minima

may be outside the experimentally accessible range of temperature so that only an ascending or descending trends are observed.

### Counter-ion Binding

The fraction of counter-ions bound to the micelle was determined conductometrically by the slope ratio method, a well proclaimed method used in the past by us and others [25–31]. In this method, the ratio of the pre and the post micellar slopes,  $S_1$  and  $S_2$ , respectively of the specific conductance versus concentration plots are considered. The ratio  $S_2/S_1$  is taken as the fraction of counter-ions dissociated from the micelle so that the fraction bound is given as  $\beta = (1 - S_2/S_1)$ . Buckingham et al. [32] showed earlier that this simple method gives a fairly quantitative estimation of  $\beta$  which is in good agreement with the electrometric (ion-selective membrane electrode) method [33, 34]. The inset in Fig. 2a shows the variation of  $\beta$  with temperature. It had been reported earlier that for SDS and CPC,  $\beta$  decreased linearly with temperature. However, for sarcosinate, the trend was different. There was a mild initial rise followed by sharp decline in  $\beta$  at temperatures  $>303$  K. Counterion dissociation was prominent at higher temperatures which was comparable with decyl trimethyl ammonium bromide [35].

### Energetics

Standard Gibbs' free energy change ( $\Delta G_m^0$ ) for the micellization process was obtained based on the phase separation model [36],

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{\text{CMC}} \quad (1)$$

where  $X_{\text{CMC}}$  is the CMC expressed in mole fraction unit, and  $R$  and  $T$  have their usual meaning. The standard state was hypothetical state of unit mole fraction.

Standard enthalpy, entropy, and specific heat changes for the micellization process were evaluated from the following equations:

$$\Delta H_m^0 = \frac{d(\Delta G_m^0/T)}{d(1/T)} \quad (2)$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (3)$$

$$\Delta C_{p,m}^0 = \frac{d(\Delta H_m^0)}{dT} \quad (4)$$

The plot between  $(\Delta G_m^0/T)$  against  $(1/T)$  was non-linear (Fig. 3). A second-degree polynomial equation of the following form was used to calculate  $\Delta H_m^0$ . Thus,

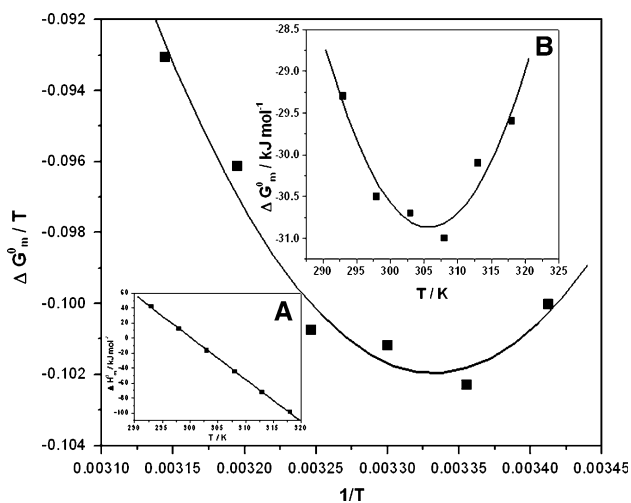
$$\frac{\Delta G_m^0}{T} = A + \frac{B}{T} + \frac{C}{T^2} \quad (5)$$

Hence,

$$\Delta H_m^0 = \frac{d(\Delta G_m^0/T)}{d(1/T)} = B + \frac{2C}{T} \quad (6)$$

where  $A$ ,  $B$ , and  $C$  are the coefficients of the polynomial. Their values were 2.81,  $-1747.93$ ,  $262264.6$ , respectively, and the correlation coefficient of the fitting curve (Fig. 3 main plot) was 0.9695.

The energetic parameters are presented in Table 1. The average values of CMC by the three methods used were taken to calculate  $\Delta G_m^0$  values. Large negative  $\Delta G_m^0$  values have indicated favorable self-aggregation of the SDDS; at and above 313 K the spontaneity slightly decreased. Enthalpy values obtained from the van't Hoff protocol [17] are also largely negative indicating an exothermic micellization process. Consequently, the entropy changes were large and negative except at  $T \leq 298$  K. Such observations for the ionic surfactants have also been reported in the past.



**Fig. 3** Plot of  $(\Delta G_m^0/T)$  vs.  $(1/T)$ , the experimental points are fitted to a non-linear two-degree polynomial curve,  $\Delta H_m^0$  values at different temperatures can be obtained from the corresponding equation. *Inset A*: Variation of  $\Delta H_m^0$  with temperature. *Inset B*: Variation of  $\Delta G_m^0$  with temperature

Normally, micelle formation ends up with an increase in entropy and water structure disruption. The micellar hydration and association of shorter chain amphiphiles may also end up with low positive and even large negative entropy changes in the process. We have considered that the hydrophobic hydration of the tail part of SDDS was modest while the head group has large positive hydration. The latter outweighed the disruption of the former to finally end up with ordering of the system as a whole. The dependence of van't Hoff derived  $\Delta H_m^0$  and  $\Delta G_m^0$  on temperature is shown in Fig. 3, insets A and B, respectively. The  $\Delta C_{p,m}^0$  value obtained from the slope of  $\Delta H_m^0$  versus  $T$  plot (inset A, Fig. 3) was  $-5.63 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . It was likely that  $\Delta H_m^0$  and  $\Delta S_m^0$  values obtained from van't Hoff will be widely different from those obtained directly from Isothermal Titration Calorimetry [37, 38]. ITC measures the integral heat of micellization whereas van't Hoff measures the differential heat of micellization, and hence there a difference occurs. ITC results (Fig. 4a) on  $\Delta H_m^0$  and  $\Delta S_m^0$  at 298, 303, and 308 K are included in Table 1 in parentheses. Large differences from van't Hoff results were observed.

### Interfacial Parameters

The surface excess of SDDS at the CMC ( $\Gamma_{\max}$ ) was obtained from the Gibbs adsorption equation:

$$\Gamma_{\max} = -\frac{1}{2.303iRT} \lim_{C \rightarrow \text{CMC}} \frac{d\gamma}{d \log C} \quad (7)$$

where, all terms having their usual meanings [29–31]. The  $d\gamma/d \log C$  was obtained from the slope of the linear surface tension ( $\gamma$ ) versus  $\log C$  plot.

The minimum area of the amphiphile head group at the surfactant saturated monolayer at the air/solution interface ( $A_{\min}$ ) was obtained from the relation:

$$A_{\min} = \frac{10^{18}}{N\Gamma_{\max}} \quad (8)$$

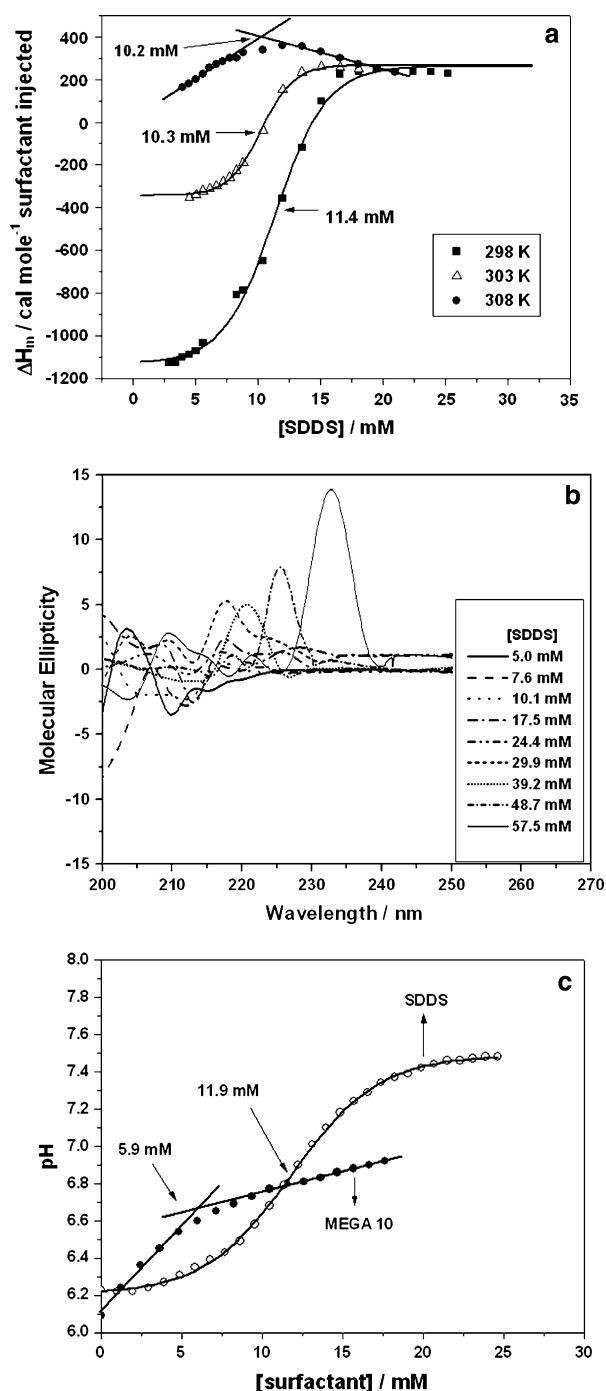
where,  $N$  is Avogadro's number.

The standard Gibbs free energy change due to adsorption ( $\Delta G_{\text{ads}}^0$ ) was obtained from

$$\Delta G_{\text{ads}}^0 = \Delta G_m^0 - \frac{\pi_{\text{CMC}}}{\Gamma_{\max}} \quad (9)$$

where,  $\pi_{\text{CMC}}$  is the surface pressure, and  $\Delta G_m^0$  is the free energy change due to micellization obtained from the tensiometric CMC values. The interfacial parameters are also presented in Table 1.

The nature of amphiphile packing in micelles and their structural geometry was estimated based on the proposition of Israelachvili [39], in terms of the packing parameter ( $P$ ):



**Fig. 4** **a** Microcalorimetric profiles of SDDS at 298, 303, and 308 K, the corresponding CMCs are shown in the figure. **b** Circular dichroism profile of SDDS, showing molecular ellipticity against wavelength at various [SDDS], the concentrations being mentioned in the figure. **c** pH vs. [surfactant] profiles for SDDS and MEGA 10 showing breaks at their respective CMCs

$$P = \frac{v}{Al_c} \quad (10)$$

where,  $l_c$  is the critical length of the hydrophobic chain of the monomer,  $A$  is the surface area of the head group and  $v$

is the critical volume of the hydrophobic chain. Both  $l_c$  and  $v$  for a saturated hydrocarbon chain with  $C_n$  number of carbon atoms can be obtained from the proposed formulas of Tanford [40]. Thus,

$$l_c = (0.154 + 0.1265C_n) \text{ nm} \quad (11)$$

$$v_c = (0.0274 + 0.0269C_n) \text{ nm}^3 \quad (12)$$

The head group area of the sarcosinate was found to be  $\sim 0.8 \text{ nm}^2$  per monomer in the lower temperature range. Above 303 K, it increased to  $\sim 0.885 \text{ nm}^2$ , probably due to stronger electrostatic repulsion between the desolvated head groups. The process of adsorption was found to be more favorable than that of micellization,  $\Delta G_m^0/\Delta G_{\text{ads}}^0 \cong 0.6$  throughout the temperature range from 298 to 313 K. Israelachvili's theory has suggested that for spherical assemblies  $P \leq 0.333$ . In this study, sarcosinate ended up with  $P$  values much lower than 0.333 at all studied temperatures, concluding that spherical micelles were formed in all the cases. This gets support as ionic surfactants in general are reported to form spherical assemblies close to their CMC values.

pH effect on CMC,  $\beta$ , interfacial properties and energetics.

The sarcosinates were reported to exhibit pH-dependent antimicrobial activities [41]. Above pH 7, they have no antibacterial or antifungal activities. At pH 5.8, they are effective against *Staphylococcus aureus*, *Streptococcus faecalis*, *Lactobacillus acidophilus*, *Trichophyton mentagrophytes*, and *Pityrosporum ovale*. At pH 4, they show strong activity against *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus mesentericus*, and many other fungi.

We have investigated the effect of pH on amphiphile behavior of SDDS in solution and at the interface. The studied pH range was 4.9 to 10.8. At  $\text{pH} \leq 4.9$ , white to off-white waxy solid to semi-solid lauroyl sarcosinic acid was found to be formed. It was insoluble in water but soluble in most organic solvents like glycols, glycerine, silicone, aliphatic hydrocarbons, etc. In the pH range of 4 to 7, the *N*-acyl sarcosinates exist in equilibrium with the free *N*-acyl sarcosinic acid. The CMC of SDDS at different studied pH (4.9–10.8) did not show any perceptible trend by tensiometry or spectrophotometry; only there was a moderate decline of CMC on going from pH 4.9 to 5.8. The values are reported in Table 2. Conductometry measurements were taken at low ionic strength ( $\mu = 0.005$ ); the results showed decreasing CMC with increasing pH. The SDDS was an anionic amphiphile, under the influence of anionic environment with increasing pH, self-aggregation of the species was promoted to make CMC decrease. The absence of a trend by both tensiometry and spectrophotometry was inexplicable.

**Table 2** pH effects on CMC,  $\beta$ ,  $P$  and energetic parameters in bulk and at the interface of SDDS at 303 K

pH	Cond (mM)	Tens (mM)	Abs (mM)	$\beta$	$\Delta G_m^0$ (kJ mol <sup>-1</sup> )	$\Gamma_{\max} \times 10^6$ (mol m <sup>-2</sup> )	$A_{\min}$ (nm <sup>2</sup> mol <sup>-1</sup> )	$\Delta G_{ad}^0$ (kJ mol <sup>-1</sup> )	$P$
4.9	14.1	11.4	15.4	0.301	-27.2	1.90	0.874	-52.2	0.240
5.8	13.5	8.42	9.18	0.496	-32.4	1.81	0.915	-52.7	0.229
6.9	12.0	10.7	9.59	0.396	-30.1	1.58	1.05	-50.5	0.199
8.6	10.2	9.13	9.14	0.388	-30.3	1.36	1.22	-51.1	0.172
10.8	9.54	11.6	10.5	0.378	-29.7	1.83	0.906	-45.5	0.231

Standard deviations in the CMC values were  $\pm 0.18$ ,  $\pm 0.16$ , and  $\pm 0.15$  for conductometry, tensiometry, and spectrophotometry, respectively.  $\beta$  values were uncertain within  $\pm 5\%$

$\beta$  was obtained following the same protocol as discussed earlier. pH 4.9 has witnessed lower  $\beta$  value than that in water (pH  $\approx 6.0$ ) (Table 2). Increase in pH from 4.9 to 5.8 produced increase in  $\beta$ , thereafter  $\beta$  slowly decreased with pH. With increasing pH, the solution had increasing  $[\text{OH}^-]$  which reduced the counter  $\text{Na}^+$  ion binding to the micelle to result in diminution of  $\beta$ . The increase in  $\beta$  from pH 4.9 to 5.8 arose from the favorable conversion of lauroyl sarcosinic acid to its sodium salt.

The standard Gibbs free energy of micellization was evaluated using the standard equation used in the earlier section. The average CMC values from all three methods were used in the calculation, however, those from conductometry alone also yielded the same trend of  $\Delta G_m^0$ . Except  $\Delta G_m^0$  (pH 5.8), all others followed a smooth two-degree polynomial fit with a regression value of  $\sim 0.98$ . The results are presented in Table 2.

The interfacial parameters like surface excess, minimum area of the head group per amphiphile molecule, free energy of adsorption and lastly, the packing parameter  $P$  were all determined using the same equations as described in the previous section and the values are also included in Table 2. The packing parameter values have supported the formation of spherical micelles at all the studied pH. The interfacial parameters had mild dependence on pH.

#### Salt Effect on Solution Behavior of SDDS

Salts may be water structure-breakers, i.e., chaotropes; or water structure-makers, i.e., kosmotropes [42, 43]. Normally, addition of salts to aqueous solutions of colloidal electrolytes results in diminution of CMC. Corrin and Harkins proved earlier that this behavior is not governed by the principle of ionic strength or the Debye–Huckel relationships [44]. Addition of salts may also cause shape transition for amphiphile aggregates or micelles. Fujio [45] reported earlier salt-induced sphere to rod transition of tetradecyl pyridinium bromide micelles in aqueous NaBr solutions, whereas dodecyl pyridinium bromide resulted in stable spherical micelles [46] (although aggregation number increased from 46 to 71) over the

whole range of the studied [NaBr] (0 to 6 M). In general, the longer the alkyl chain, the lower is the threshold salt concentration required for the sphere-rod transition. Salts like sodium salicylate and sodium benzoate, etc... are known to affect micellar morphologies of cationic surfactants in solution [47–49].

We have herein attempted to study the salt effect on the micellization behavior of SDDS. The salts used were LiCl, NaCl, KCl, CsCl, NaBr, NaI, and  $\text{NaN}_3$ . The extent of hydration of the cations followed the order  $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$ , and that of the anions was  $\text{I}^- < \text{Br}^- < \text{Cl}^-$ .

The effect of increasing [NaCl] was studied in the range of 0.005–0.1 M. From [salt]  $\geq 0.01$  M, the CMC was observed to decrease significantly due to compression of the electrical double layer (Table 3). The CMC—[salt] profiles have yielded well-fitted polynomials, the equation obtained for conductometry,

$$\text{CMC} = 12.939 - 0.377[\text{salt}] + 0.006[\text{salt}]^2 (R = 0.999) \quad (13)$$

and that for tensiometry,

$$\text{CMC} = 13.727 - 0.205[\text{salt}] + 0.0011[\text{salt}]^2 (R = 0.985) \quad (14)$$

Although CMC decreased conveniently with increasing [NaCl], the micellar shape remained almost constant throughout the studied range of NaCl concentration (to be discussed later). The CMC values by spectrophotometry showed wide differences up to 10 mM; at higher [NaCl] the agreements with tensiometry were good. The absorbance results were not considered in testing the correlations presented for the other two methods. The effect of varying salts was studied at two salt concentrations, 0.01 and 0.025 M, in all cases tensiometry results were higher than conductometry. By salt effect the CMC of SDDS decreased as is usually observed (Table 3).

The effect of ions on the CMC may be looked into in the light of the “Hoffmeister Series” (HS) or Hoffmeister effect [50–52]. Considering the CMC reducing activity of the ions comparable with the salting out phenomenon of water soluble polymers, proteins, and polyelectrolytes,

**Table 3** Effect of NaCl on CMC,  $\beta$ ,  $\Delta G_m^0$ ,  $\Gamma_{\max}$ ,  $A_{\min}$  and  $P$  of SDDS at 303 K

[NaCl] (mM)	Cond (mM)	Tens (mM)	Abs (mM)	$\beta$	$\Delta G_m^0$ (kJ mol <sup>-1</sup> )	$\Gamma_{\max} \times 10^6$ (mol m <sup>-2</sup> )	$A_{\min}$ (nm <sup>2</sup> mol <sup>-1</sup> )	$P$
0	12.9	13.2	11.7	0.430	-30.2	2.45	0.679	0.308
5	11.3	13.2	9.82	0.376	-29.4	2.47	0.671	0.312
10	9.70	12.3	8.47	0.393	-30.2	2.63	0.631	0.332
25	7.70	8.84	7.84	0.582	-35.3	2.12	0.783	0.267
50	–	5.94	5.73	–	–	1.98	0.840	0.249
75	–	5.15	4.49	–	–	2.00	0.831	0.252
100	–	4.16	3.46	–	–	1.40	1.19	0.177

Standard deviations in the CMC values were  $\pm 0.18$ ,  $\pm 0.16$ , and  $\pm 0.15$  for conductometry, tensiometry, and spectrophotometry, respectively.  $\beta$  values were uncertain within  $\pm 5\%$

the effectivity should follow the order, for anions:  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  and for cations:  $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . We have observed the order of effectivity of the cations to be opposite to the HS requirement as also reported recently by Chakraborty et al. [35]. For SDDS, an anionic surfactant as the hydrodynamic radius ( $R_H$ ) hence the ionic volume decreased from  $\text{Li}^+$  to  $\text{Cs}^+$ , chances of their association with the anionic micelles of  $\text{DDS}^-$  species should decrease with decreasing CMC. But the findings were reverse. The anions  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  have not evidenced any perceptible effect on the CMC which was also not expected for the anionic micelle studied here. It may be pointed out that in presence of 0.025 M CsCl, onset of turbidity was observed in the SDDS solutions; the system became stable at higher [CsCl] addition.

$\beta$  values in salt solutions were also determined by the slope ratio method discussed in the previous section. The determination of  $\beta$  in presence of salt with same and different counterions is not a straightforward proposition. With the addition of higher concentration of NaCl in the system, more  $\text{Na}^+$  ions (counterions) became associated

with the micellar surface with the ‘Stern layer’ causing  $\beta$  to increase. In presence of other salts like LiCl, KCl, CsCl, etc., less hydrated ions condensed more than a large solvated ion like  $\text{Li}^+$ ; the order followed the Hoffmeister series  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ . NaBr and  $\text{NaN}_3$  at 25 mM produced comparable  $\beta$ , whereas NaI produced a much lower  $\beta$ . The coion  $\text{I}^-$  produced an unusual effect on  $\beta$ . With increasing [NaCl],  $\beta$  increased with an initial slight decrease at 5 mM (Table 3). LiCl, KCl, and CsCl also produced similar effects. With increasing salt concentration more counterions became available in the shrunken electrical double layer surrounding the micelles. The order of  $\beta$  followed the sequence  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ . As the  $R_H$  decreased, counterions could approach the micelles better to undergo condensation. In comparison, among NaCl, NaBr, and NaI,  $\beta$  decreased with increasing  $R_H$  of the coions  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . This could be rationalized from the polarizability differences of the coions. The polarizability increased in the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . The higher the polarizability, the lower was the  $\beta$ . The results are presented in Table 4.

**Table 4** Salt effect on CMC,  $\beta$ ,  $\Delta G_m^0$ ,  $\Gamma_{\max}$ ,  $A_{\min}$  and  $P$  of SDDS at 303 K

Salts	Cond (mM)	Tens (mM)	Abs (mM)	$\beta$	$\Delta G_m^0$ (kJ mol <sup>-1</sup> )	$\Gamma_{\max} \times 10^6$ (mol m <sup>-2</sup> )	$A_{\min}$ (nm <sup>2</sup> mol <sup>-1</sup> )	$P$
10 mM								
LiCl	10.8	12.5	7.34	0.358	-29.0	1.91	0.871	0.240
NaCl	10.9	13.3	8.47	0.402	-30.1	2.64	0.628	0.334
KCl	11.1	13.6	11.3	0.415	-30.0	2.33	0.713	0.294
CsCl	11.9	13.9	10.5	0.441	-30.6	2.00	0.831	0.252
25 mM								
LiCl	7.80	10.5	7.11	0.388	-30.4	2.15	0.772	0.271
NaCl	7.70	11.4	7.84	0.578	-34.7	1.93	0.862	0.243
KCl	8.60	12.6	8.81	0.655	-35.7	2.60	0.639	0.328
CsCl	9.80	12.8	9.01	0.529	-33.0	1.90	0.874	0.240
25 mM								
NaBr	7.61	9.55	6.29	0.454	-32.1	2.23	0.744	0.282
NaI	7.70	10.6	7.97	0.283	-28.3	2.05	0.810	0.259
$\text{NaN}_3$	7.98	10.0	8.86	0.425	-31.4	1.63	1.02	0.205

Standard deviations in the CMC values were  $\pm 0.18$ ,  $\pm 0.16$ , and  $\pm 0.15$  for conductometry, tensiometry, and spectrophotometry, respectively.  $\beta$  values were uncertain within  $\pm 5\%$



Salts have varying effects on CMC,  $\beta$ , micellar size and shape, etc. It is then expected that the micellar aggregation number ( $n$ ) would also be affected with salt addition. The growth of SDS micelles is known to depend on the counterions, the coions nominally affect the micellar growth. Fujio [45] and Aswal and Goyal [53] have reported greater efficacy of KBr/NaBr over KCl/NaCl in affecting the micellar properties viz. aggregation numbers, viscosity, etc. We observed that increasing [NaCl] did affect the CMC while the aggregation number (determined by the method of static fluorescence quenching [29–31] using pyrene as the probe and C<sub>16</sub>PC as the quencher) remained unaffected. The micellar polarity as determined using the  $I_1/I_3$  ratio of pyrene was also found to remain almost constant in the presence of various salts; increasing [NaCl] did not produce any distinct effect (Table 5). There was no shape transition either as revealed from the calculated  $P$  values (discussed subsequently). At [salt] = 25 mM and [SDDS] = 90 mM, the salt effect on  $n$  was studied. Increasing [SDDS] from 100 to 200 mM produced increased  $n$  from 81 to 127. Increased [NaCl] from 5 to 100 mM had a minor effect on  $n$ . Sodium halides also produced minor changes of  $n$ . Chlorides of Li, Na, K, and Cs evidenced a mild increase in  $n$  excepting Na which produced a lower value. The results are also shown in Table 5. On the whole, the studied salts had minor effect on the  $n$  and  $I_1/I_3$  values of SDDS micelles.

$\Gamma_{\max}$ ,  $A_{\min}$ , and the  $P$  values of SDDS under the influence of salts are given in Tables 3 and 4. The  $\Gamma_{\max}$  and  $A_{\min}$  values were inversely dependent as expected. The  $P$  values have shown that under the influence of the salts, the micellar geometries of SDDS were all spherical.

#### Comparison of SDDS with *N*-Methyl-*N*-Decanoyl Glucamide (MDGA)

With reference to the study on SDDS, an attempt was made to compare its physicochemistry with MDGA, a biodegradable alkylpolyglucoside surfactant, because of structural similarities between these two amphiphiles. Both

have a secondary amide linkage at the juncture of the polar head and the non-polar tail.

The detailed thermodynamic study of MDGA was conducted at several temperatures by the ITC method [19], where the enthalpy–concentration profiles produced first order transitions in the pattern, and the transition points were taken as the CMC. Below 303 K, the micellization of MDGA 10 was endothermic and exothermic above it. SDDS has also shown such a feature but at a slightly higher temperature, namely 308 K (Fig. 4a).

The thermodynamic parameters for micellization of SDDS may be deciphered for estimating the contributions of the terminal methyl group, the intermediate methylenes and the hydrophilic head group as has been done for MDGA [54]. The additivity protocol was the same as used earlier [55, 56],

$$\Delta G_m^0 = \Delta G_m^0(\text{hy}) + (n_c - 1)\Delta G_m^0(\text{CH}_2) + \Delta G_m^0(\text{CH}_3) \quad (15)$$

where  $\Delta G_m^0(\text{hy})$ ,  $\Delta G_m^0(\text{CH}_2)$ , and  $\Delta G_m^0(\text{CH}_3)$  are the free energy contributions of the head group, the intermediate methylene groups and the terminal methyl group respectively and  $n_c$  is the number of CH<sub>2</sub> groups present in the hydrophobic tail. For SDDS,  $n_c = 11$  with –CH<sub>2</sub>–CO–N(CH<sub>3</sub>)–CH<sub>2</sub>–CO<sub>2</sub>– as the head group. The terminal CH<sub>3</sub> group and the intermediate –CH<sub>2</sub>– groups experience almost comparable environment in both the amphiphiles. We have considered  $\Delta G_m^0(\text{CH}_3) = -8.78 \text{ kJ mol}^{-1}$  and  $\Delta G_m^0(\text{CH}_2) = -2.9 \text{ kJ mol}^{-1}$  considering the rationale of Okawauchi et al. [54]. Thus, in the data treatment at 303 K,  $\Delta G_m^0(\text{hy})$  for SDDS was observed to be  $+6.98 \text{ kJ mol}^{-1}$  which was comparatively lower than that of MDGA ( $+13.6 \text{ kJ mol}^{-1}$  on an average within the temperature range 293–318 K). This was quite expected since the head group of MDGA was more hydrophilic than the head group of SDDS thereby resulting in higher non-spontaneous transfer of free energy from the bulk phase to the micellar phase.

Akisada et al. [57] earlier showed that MDGA gives a peak in the CD spectra after micellization. Upon

**Table 5** Aggregation number and polarity of SDDS micelles in salt solution

[Sarcosinate] (mM)	100	150	200						
$n$	81	115	127						
$I_1/I_3$	1.078	1.086	1.061						
[NaCl] (mM)	5	10	25	75	100				
$n$	82	80	76	75	76				
$I_1/I_3$	1.068	1.075	1.015	1.004	0.919				
Other salts (25 mM)	NaCl	NaBr	NaI	NaN <sub>3</sub>		LiCl	NaCl	KCl	CsCl
$n$	76	89	84	86		89	76	94	91
$I_1/I_3$	1.015	0.926	0.925	1.013		1.068	1.015	1.078	1.074

micellization, the carbonyl moieties become arranged within the micellar sphere so that the  $-C=O$  group of the adjacent hydrophobic chains come within close proximity of each other and the peak in CD spectra arises from the Cotton effect due to the  $n-\pi^*$  transition of the carbonyl group. The peak intensity increased slightly with MDGA concentration and ultimately saturated at a much higher concentration. CD spectra of SDDS were also taken at concentrations varying from below to above CMC (Fig. 4b). We also obtained a peak from and above the CMC, with the peak height increasing with [surfactant], and slight shift in the peak maximum. The conformational conditions for both the surfactants were found to be comparable.

An interesting observation was noted on the effect of SDDS and MDGA addition in water with respect to their effects on the pH of the solutions. The stable surfactants like SDS, cetyl trimethyl ammonium chloride, etc., do not show changes in pH of their aqueous solutions, which MDGA and SDDS did. MDGA on gradual addition to water showed a continuous increase in pH, the break point corresponded nicely with the CMC. The SDDS when added to water produced a prominent sigmoidal curve, the inflexion point of which corresponded very closely to its CMC (Fig. 4c). It was also cross-checked by dilution of SDDS with water. This aspect warrants further investigation in future.

Before we conclude, we consider presentation of physicochemical behaviors of the dodecanoyl sarcosinic acid (HDDS) which are considered relevant and interesting.

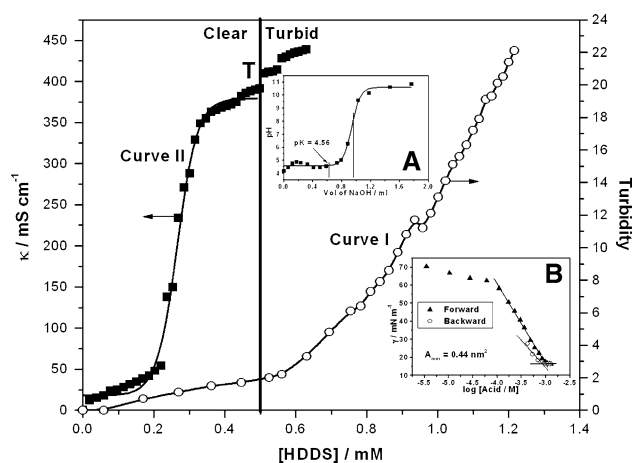
#### Physicochemical Behavior of Dodecanoyl Sarcosinic Acid (HDDS)

Literature reports have indicated that acid forms of acyl sarcosines are equally surface active, in fact interfacial adsorption increases at lower pH [8]. For clarity of understanding, we elucidated the structure of the precipitate obtained at lower pH. For the sodium salt, MS (ESI)  $m/z$ : Calculated for ( $M^+ + Na$ ) 317.38, Found 316.20 and for the acid MS (ESI)  $m/z$ : Calculated for ( $M^+ + Na$ ) 294.39, Found 294.32. Moreover, the IR spectrum of the sodium-salt and the precipitate when compared, confirmed that the precipitate was a very pure form of the acid. The amide carbonyl stretching frequency was recorded at  $1,610\text{ cm}^{-1}$  in both the spectra. The carbonyl of the sodium-salt stretched at  $1,631\text{ cm}^{-1}$ ; due to resonance the bond order in this case was less than two, but the carbonyl of the acid form having greater electron density stretched at  $1,734\text{ cm}^{-1}$ . In addition to these, the broad band around  $2603.5\text{ cm}^{-1}$  was due to the hydrogen bonded O–H stretching frequency in the dimeric form of the acid. Further analysis of the freeze-dried acid sample was done

to confirm its purity. The calculated and observed values for the acid were: C, 66.38; H, 10.77; N, 5.16; Found: C, 66.08; H, 15.76; N, 5.04. Except H, C, and N were perfectly matching. The excess hydrogen was considered due to the presence of moisture trapped in the sample, which was found to be hard to remove even under high pressure vacuum for several hours followed by desiccating for several days. It has been observed that anhydrous  $\text{CuSO}_4$  having a high affinity for water abstraction for crystallization could only weakly remove the trapped water from HDDS. It was considered that the excess moisture corresponded to 12 molecules of water necessary for the crystallinity of the acid HDDS. It was also supported by the result of the freeze drying method which was unable to remove the water of crystallization.

The structure of the precipitate obtained at low pH has been thus confirmed to be that of the acid. It was a moderately strong organic acid, with  $pK = 4.56$  (Fig. 5, inset A) obtained from the half-neutralization point of the titration curve, the value was between those of simple fatty acids and alkyl sulfuric acids or alkyl aryl sulfonic acids.

The acid has poor solubility in water, which was found to be  $0.5\text{ mM}$  (at T) by turbidity experiments (Fig. 5, curve I). The conductance profile was conspicuous in this respect (Fig. 5, curve II). The acid solution was weakly conducting up to  $\sim 0.26\text{ mM}$ , above which the conductance sharply increased to yield a sigmoidal course. The experiment was repeated a number of times to check reproducibility. The conductance value steadily increased up to the solubility limit (marked with the dropped perpendicular meeting the turbidity course at T), above which the acid phased out (or was insoluble) making the conductance values unsteady.



**Fig. 5** Physicochemical characterization of the acid form of SDDS, *Curve I*: Turbidity profile of the acid. *Curve II*: Conductometric profile of the acid. *Inset A*: pH-metric titration profile of a known strength of the acid to determine the  $pK$  value. *Inset B*: Tensiometric profile of the acid

Below 0.26 mM, the concentration of ions in solution was low to contribute perceptible conductance; above 0.26 mM, the acid contributed more ions through dissociation resulting in a conductance jump like a cooperative process which reached to its maximum at T owing to distinct insolubility. Tensiometric results (Fig. 5, inset B) have produced a break at 0.87 mM, much higher than 0.5 mM realized from both conductometry and turbidimetry. It was possible that in tensiometry after reaching the solubility limit at 0.5 mM, the more surface active undissociated HDDS occupied the air/water interface to reduce  $\gamma$  and eventually showing a break at a higher concentration than 0.5 mM.

Detailed studies on the physicochemical behaviors essentially interfacial and bulk behaviors of sodium dodecanoyl sarcosinate (SDDS) were made. Effects of salt, temperature and pH on the self-association and related properties of SDDS with reference to thermodynamics of the process were undertaken, and correlation of the results in terms of physicochemical relations and concepts was attempted. A comparison of the results with another important biological polyglucoside surfactant (MDGA) was made, and the contributions of the terminal methyl group the intermediate methylene groups as well as the water soluble head group towards the free energy of micellization were estimated following a scheme used by us and Sugihara on MDGA. The acid form of the compound (HDDS) was found to have a strong water retention capability, and a pK value of 4.56 intermediate between simple fatty acids and alkyl sulfuric or alkylaryl sulfonic acids. Its water solubility was found to be 0.5 mM at 303 K. The counterion effects on the CMC of SDDS followed a reverse Hoffmeister series trend for counter cations, i.e.,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$  (preferential micelle forming sequence), whereas the counterion binding trend obeyed the Hoffmeister series requirement, i.e.,  $\beta$  increased in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ . The SDDS produced alkalinity in aqueous solution and the pH dependence formed a prominent inflexion which corresponded to its CMC, this was an unusual observation; such an effect in a mild form has been witnessed for MDGA. From CD spectra, like MDGA, conformational change manifesting a Cotton effect by way of  $\pi-\pi^*$  transition of the carbonyl group has been witnessed for SDDS. The study has produced several uncommon features whose further exploration is contemplated to be undertaken in future in our laboratory.

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