

# Systematic Studies of Sodium $\gamma$ -Octyl Aspartate to evaluate its Biodegradation, Surface Parameters, Micellization Aspects and Thermodynamic Properties of its Binary Mixture using Electrolytes

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## Abstract

$\gamma$ -octyl aspartate has been synthesized with 46.2% yield. The optimized conditions for esterification of aspartic acid and n-octanol are 24 hours duration and 1:1 molar ratio of reactants (aspartic acid: n-octanol). FT-IR,  $^1\text{H}$  NMR and CHNS element analysis techniques are used for structure elucidation of  $\gamma$ -octyl aspartate. Surface/ interfacial studies, micellization aspects, thermodynamic parameters, biodegradability and binary salt behaviour of sodium  $\gamma$ -octyl aspartate have been studied.

The CMC of synthesized surfactants was 0.0078 mol/L, whereas minimum surface area per surfactant molecule was calculated as  $29.49 \text{ \AA}^2\text{m}^2$ ; calculated aggregation number was 34 and micelle radius ( $r$ ) found to be 1.40 nm. The degree of counter-ion dissociation ( $\alpha$ ) was determined to be 0.86. Thermodynamic parameter - standard free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) was calculated as -18.70 kJ/mol. The shape of micelle of synthesized surfactant was noticed to be spherical but during binary studies in some cases, it was found to be cylindrical. OECD and Winkler's method were used to determine biodegradation of sodium  $\gamma$ -octyl aspartate found to be 95.1 %.

**Keywords:** Biodegradation, Standard free energy of adsorption, Minimum surface excess, Binary mixture and Packing parameter.

## Introduction

Most of the cleansing formulations are based on adequate quantity of surfactant granules. As the need of washing/ cleansing/ personal care product/ cosmetics keeps increasing, by the same time a desire of eco-friendly/ biodegradable surfactant granules is on high demand. Researchers of the world are trying to make safer/ mild/ biodegradable surfactant granules for sustainable environment.<sup>8,15,18</sup>

In the vast kingdom of surfactants, amino acid based surfactants are one of the hopes to make safer and less toxic surfactant moieties. The high yield preparations of amino acid based surfactant is always a hurdle in commercialization of amino acid based surfactants.<sup>9,29</sup>

A comprehensive study to illustrate all possible aspects of amino acid-based surfactant granules viz. micellization, interfacial properties, thermodynamic properties, yield improving methodology for preparation is highly desired. It will give an impetus to carry out a systematic study to understand all above mentioned aspects for sodium  $\gamma$ -octyl aspartate.

## Material and Methods

In this study, all reagents and chemicals were used without any further purification. L- aspartic acid (98.5 %), n-octanol (99.0 %), tert-butanol (98.5 %), tri-ethylamine (99.0 %) and potassium chloride (99.0%), benzophenone (99.0%) were procured from LOBA Chemie Pvt. Ltd., Mumbai (India). Sulphuric acid (98.0 %) was purchased from Merck Specialities Pvt. Ltd., Mumbai (India). Sodium chloride (99.5 %) and sodium salicylate (99.0 %) were obtained from SD Fine-Chem Limited, Mumbai (India). Pyrene (98%) was purchased from Sigma-Aldrich Chemie GmbH, Ried-str. Steinem. Absolute ethanol (99.9%) was procured from Changshu Yangyuan Chemical, China.

**Synthesis of  $\gamma$ - Octyl Aspartate:** Synthesis of  $\gamma$ - Octyl Aspartate<sup>12</sup> has one step esterification between aspartic acid and n-octanol. Several batches have been carried out to optimize the impact of molar ratios (aspartic acid and n-octanol) and effect of increase duration (hours) of esterification on yield of final product. The temperature of esterification was kept 65 °C in all studied batches. This temperature was chosen because tert-butanol was used as a solvent. More than 65 °C would not be a favourable condition for effective esterification. Table 1 and 2 clearly indicate the effect of molar ratios and duration of esterification on yield of synthesized  $\gamma$ -octyl aspartate.

A three-necked flask equipped with a magnetic stirrer, thermometer and water reflux condenser was used having 4 gm (30 mmol) aspartic acid and 4.5 ml (30 mmol) n-octanol dissolved in (50 ml) tert- butanol with continuous stirring till 45°C. After that 2.4 ml  $\text{H}_2\text{SO}_4$  was added by a syringe at 45°C, addition of  $\text{H}_2\text{SO}_4$  was noticed to be an exothermic reaction, as temperature rose to 55°C. Once  $\text{H}_2\text{SO}_4$  was added, then content of flask were stirred for desired duration viz. 04, 08, 12, 16, 24, 28 and 32 h. The highest yield i.e. 46.2 % was noticed for 24 hours duration of esterification when the molar ratio for aspartic acid: n-octanol was 1:1 (it is optimized as per data shown in table 1). The esterification reaction has shown in scheme 1.

The recovery of final product requires a lot of care and stoichiometric addition of chemicals to get pure product. A path followed for this is: 6.4 ml of tri-ethyl amine was added to neutralize  $\text{H}_2\text{SO}_4$ . After that 25 ml methanol was added at lower temperature at about  $45^\circ\text{C}$ . A suspension has been filtered and filtered mass slurred with hot water ( $60^\circ\text{C}$ ). Again was slurred mass was filtered and recrystallized by 25 ml methanol followed by 25 ml water. Obtained  $\gamma$ - octyl aspartate was dried in oven at  $50^\circ\text{C}$  for 3 hours. The yield of synthesized product was 3.4 gm and 46.2%.

#### Preparation of Sodium $\gamma$ - Octyl Aspartate (SGOA):

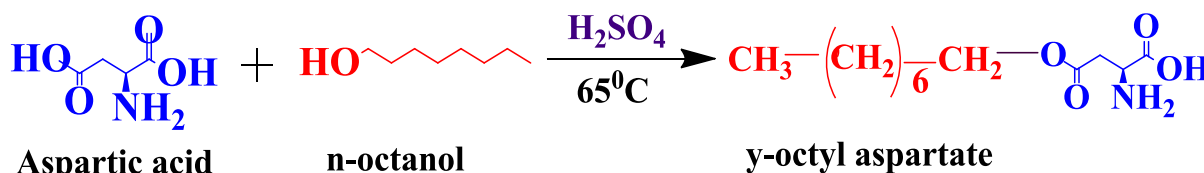
Being an organic compound,  $\gamma$ - Octyl aspartate is partially soluble in water and insoluble in many other solvents. Therefore, it was converted to water soluble via following procedure:

3.3gm (0.01 mol) of  $\gamma$ -octyl aspartate was dissolved and stirred with 35 ml of ethanol for 15 minutes. An aqueous solution of NaOH 4 ml (0.01 mol) 10% (wt. %) was added drop by drop into ethanolic solution of synthesized product.<sup>20</sup> The solution turned into a white solid mass. This

solid mass was filtered and dried. 2.67 gm white solid was obtained and the yield was 81.8 %.

**Structure elucidation:** Confirmation of structure of all synthesized products is a prime aspect of research. Without structure elucidation, no further work is possible. Therefore, instrumental analysis viz. CHNS analysis,  $^1\text{H}$  NMR and FT-IR of  $\gamma$ -octyl aspartate were carried out at Sophisticated Analytical Instrument Facility (SAIF), STIC, Cochin, Kerala (India).

**Du Nouy Tensiometer:** Du Nouy Tensiometer (Jencon, India) was used to determine the surface tension ( $\gamma_{\text{CMC}}$ ) at the air/solution interface of the sodium  $\gamma$ -octyl aspartate with the help of platinum ring detachment method. Double-distilled water (DDW) was used for the calibration of the Du Nouy Tensiometer. Platinum ring was washed by DDW and dried before each observation. The CMC value was determined by plotting the breakpoint of the surface tension against the concentration curve. The accuracy of the result was  $\pm 0.1$  dyne/cm. All the measurements were carried out at room temperature.



Scheme 1: Synthesis of  $\gamma$ -octyl aspartate by esterification reaction between aspartic acid and n-octanol.

Table 1  
Effect of molar ratios of aspartic acid and n-octanol on esterification.

| Fixed Parameters                    |                                           |            |           |
|-------------------------------------|-------------------------------------------|------------|-----------|
| 1. Temperature = $65^\circ\text{C}$ |                                           |            |           |
| 2. Duration = 4 hours               |                                           |            |           |
| S.N.                                | Molar Ratio<br>Aspartic acid : n- octanol | Yield (gm) | Yield (%) |
| 1.                                  | 1:1.00                                    | 2.7        | 36.7      |
| 2.                                  | 1:1.25                                    | 2.4        | 32.6      |
| 3.                                  | 1:1.50                                    | 2.2        | 29.9      |
| 4.                                  | 1:1.75                                    | 1.7        | 23.1      |

Table 2  
Impact of duration of esterification on yield of  $\gamma$ -octyl aspartate ( $\gamma$ -OA)

| Fixed Parameters                                   |                      |            |           |
|----------------------------------------------------|----------------------|------------|-----------|
| 1. Molar ratio (1:1.00) = aspartic acid: n-octanol |                      |            |           |
| 2. Temperature = $65^\circ\text{C}$                |                      |            |           |
| S.N.                                               | Time duration (Hour) | Yield (gm) | Yield (%) |
| 1.                                                 | 04                   | 2.7        | 36.7      |
| 2.                                                 | 08                   | 2.7        | 36.7      |
| 3.                                                 | 12                   | 2.9        | 39.4      |
| 4.                                                 | 16                   | 3.0        | 40.8      |
| 5.                                                 | 24                   | 3.3        | 44.9      |
| 6.                                                 | 28                   | 3.2        | 43.5      |
| 7.                                                 | 32                   | 2.9        | 39.4      |

**Conductivity Method:** The critical micelle concentration (CMC) of binary solutions was determined by using automatic digital conductivity meter (Metzer, METZ-1001 M; Mathura, India) having cell constant  $1.01 \text{ cm}^{-1}$ . KCl solution was used for the calibration of conductivity measurement. The CMC of the binary solution depends upon the mobility and number of ions or charged particles present in the solution. The CMC values were obtained from break through point of the graph between conductivity versus concentration of SGOA and its binary mixtures with inorganic and organic electrolytes.

**Micellization parameters:** The steady-state fluorescence quenching method using RF-5301 PC Shimadzu (Japan) spectrophotometer with a slit width of  $1.25 \text{ nm}$  was used to investigate all micellization parameters in this study. Aggregation number, pyrene intensity, apparent dielectric constant, micelle radius, surface area per head group, packing parameters and shape of micelle of pure and mixed micelle were calculated from the various spectra of spectrophotometer. Pyrene and benzophenone were used as probe and quencher respectively. Pyrene intensity was excited at  $335 \text{ nm}$  and emission spectra were scanned at  $340$  to  $600 \text{ nm}$ . All emission and excitation spectra were observed at room temperature.

Turro and Yekta<sup>17</sup> proposed a method to determine the aggregation numbers based on Tachiya model.<sup>28</sup> The aggregation numbers were calculated using the following equation.

$$\ln \frac{I_1}{I_q} = \frac{N \cdot Q}{(C - \text{CMC})} \quad (1)$$

$$\frac{I_1}{I_q} = \frac{\exp Q}{\text{mic}} \quad (2)$$

$$N = \frac{(C - \text{CMC})}{\text{mic}} \quad (3)$$

where  $I_q$  and  $I_o$  = Fluorescence intensities with or without quencher,  $Q$  = Concentration of used quencher,  $N$  = Aggregation numbers,  $\text{CMC}$  = Critical micelle concentration and  $C$  = Concentration of the surfactant/ binary mixture.

A pyrene solution of  $1 \times 10^{-3} \text{ M}$  concentration is prepared by dissolving  $0.02 \text{ gm}$  pyrene in  $100 \text{ ml}$  of ethanol. Then  $1 \text{ ml}$  of this probe solution is dissolved in  $200 \text{ ml}$  of ( $3 \times \text{CMC}$ ) SGOA aqueous solution to get pyrene concentration  $1 \times 10^{-6} \text{ M}$ .<sup>1, 19</sup>

Basically, quencher was playing a role in reducing the fluorescence intensities. Fluorescence intensities were decreased by the interaction of the excited state of the

fluorophore with quencher present in the nearby surrounding of probe. Four different concentrations of quencher viz.  $2 \times 10^{-4} \text{ mol/L}$ ,  $4 \times 10^{-4} \text{ mol/L}$ ,  $6 \times 10^{-4} \text{ mol/L}$  and  $8 \times 10^{-4} \text{ mol/L}$  were used to calculate mic value by using equation 3.<sup>34</sup>

**Electrolytes effect on the micelle of sodium  $\gamma$ -Octyl aspartate:** All studied parameters clearly revealed that micelles of the SGOA were influenced substantially by the addition of electrolytes (sodium and potassium having inorganic and organic salts). NaCl and KCl are used as inorganic electrolytes: sodium benzoate (NaBenz) and sodium salicylate (NaSal) were used as organic electrolytes to study their effect on the micelle of SGOA. The concentration range of electrolytes used was  $10^{-3}$  to  $10^{-1} \text{ M}$ .

**Evaluation of biodegradability:** Being amino acid based compound, SGOA would be biodegradable. Its biodegradation has been carried out by OECD<sup>21</sup> and Winkler's<sup>15</sup> method. The biodegradation of SGOA was carried out in anaerobic conditions.

**Anaerobic process:** The organic matter converts into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and unstable side products such as  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$  in the absence of oxygen.

The following expression has been used for calculating biodegradation of SGOA:

$$\text{Biodegradation}(\%) = \frac{\text{Biological Oxygen demand (BOD)}}{\text{Theoretical Oxygen Demand (ThOD)}} \quad (4)$$

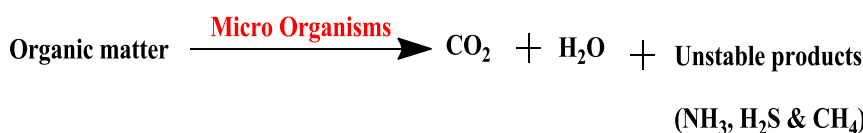
BOD was calculated by using following expression:

$$\text{BOD} = D^0 - D^7 \times \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} \text{ mg / L} \quad (5)$$

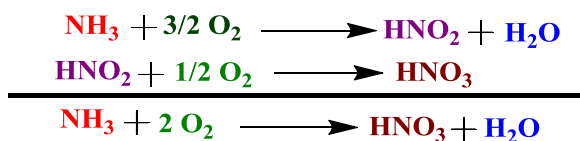
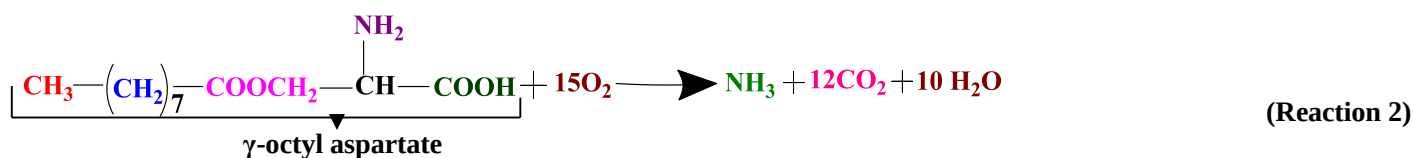
where  $D^0$  = Dissolved oxygen (DO) of the sample in  $\text{mg/L}$  at 0<sup>th</sup> day (at the start of the experiment) and  $D^7$  = Dissolved oxygen (DO) of the sample in  $\text{mg / L}$  after 7<sup>th</sup> day.

Theoretical oxygen demand (ThOD) was calculated.<sup>27</sup> The carbonaceous and Nitrogenous oxygen demand are discussed below:

- **Carbonaceous oxygen demands for SGOA:** Total organic carbon and nitrogen are converted into carbon dioxide ( $\text{CO}_2$ ) and ammonia ( $\text{NH}_3$ ) respectively.
- **Nitrogenous oxygen demands for SGOA:** Entire ammonia got oxidized consecutively to nitrite and then nitrate. The balanced reactions are as follows:



(Reaction 1)



## Results and Discussion

**Synthesis of  $\gamma$ -Octyl aspartate:**  $\gamma$ -octyl aspartate has been synthesized with minute variation in reaction parameters as reported in literature.<sup>12</sup> Table 1 illustrates the effect of higher molar ratio of n-octanol with respect to aspartic acid. Four different batches were carried out having aspartic acid: n-octanol ratio i.e. 1:1.00, 1:1.25, 1:1.50 and 1: 1.75. All four batches of esterification were conducted at 65°C; tert-butanol is used as a solvent. On the perusal of the results of table 1, 36.7 % yield is obtained for lowest molar ratio i.e. 1: 1.00 of reactants. Further, data of table 1 clearly indicates that rise in molar quantity of n-octanol has not given any increase in the yield of  $\gamma$ -octyl aspartate, rather showed a decreasing trend. A tentative reason of decrease in yield can be due to the starting of backward reaction at higher molar quantities of n-octanol.

After optimizing molar quantities, now the duration of esterification was to be optimized. For this, seven different durations were studied i.e. 04, 08, 12, 16, 24, 28 and 32 hours. During these batches, two reaction parameters were kept constant i.e. molar ratio of reactant (1:1.00) and temperature of the esterification i.e. 65°C. There was no difference at 04 and 08 hours duration of esterification, the yield i.e. 36.7 % in both the cases after that gradual rise in the yield have been observed and highest yield (46.2%) was

found when reaction has been carried out for 24 hours (1 day).

Two more batches were also conducted out but no increase in the yield was noticed, rather it decreased. The reason for decrease in the yield could be start in the decomposition of ester. As a result, 1:1 molar ratio of reactant, 65 °C temperature and 24 hours duration are favourable esterification parameters for sustainable yield of  $\gamma$ -octyl aspartate.

## Structure Characterization of synthesized $\gamma$ -Octyl aspartate

**CHNS analysis:** Carbon(C), hydrogen (H) and nitrogen (N) were analyzed by Sophisticated Analytical Instrument Facility (SAIF), STIC, Cochin, Kerala and evaluated values are: C (58.82 %), H (9.46 %) and N (5.71 %) whereas calculated values are C (58.07 %), H (9.39 %) and N (5.09 %). This analysis helps to confirm the molecular formula of synthesized compound to be  $\text{C}_{12}\text{H}_{23}\text{O}_4\text{N}$ .

**Interpretation of  $^1\text{H}$  NMR:** The  $^1\text{H}$  NMR spectra of  $\gamma$ -octyl aspartate are shown in figure 1.<sup>33</sup> Spectra were carried at 400 MHz in  $\text{D}_2\text{O}$ ,  $\delta$  in ppm. Important illustrated protons are as follows: 1.079 [s, 3H,  $\text{CH}_3$ ], 1.095 [10H,  $(\text{CH}_2)_5$ ], 2.856 [m, 4H,  $(\text{CH}_2)_2$ ], 3.978 [t, -CH ( $\text{COOH}$ )], 7.907 [2H,  $\text{NH}_2$ ], 4.007 [s, 1H, CH-O-C=O].

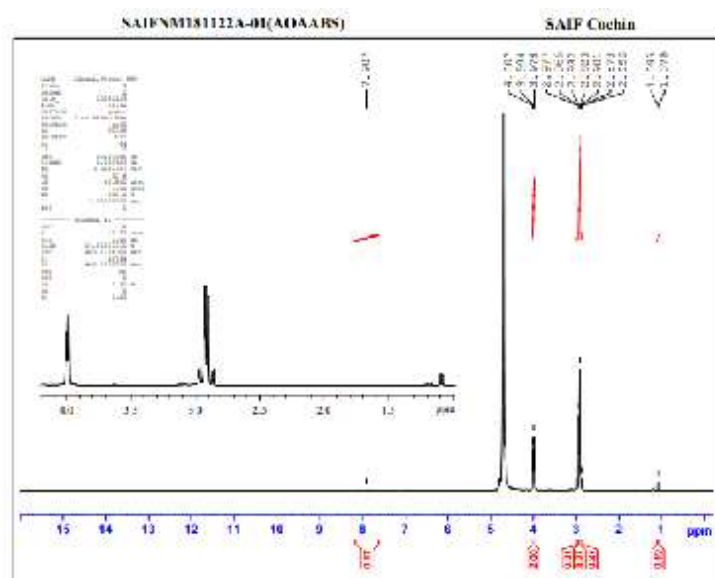


Figure 1:  $^1\text{H}$  NMR spectra of  $\gamma$ -octyl aspartate

**Peak analysis of FT-IR:** The functional groups were confirmed by employing Fourier transform infrared spectroscopy (FT-IR) in the range 4000-400  $\text{cm}^{-1}$  using KBr pellets. The FT-IR spectra of  $\gamma$ -octyl aspartate<sup>33</sup> is shown in figure 2. All important peaks that confirm the presence of certain functional groups are as follows: a (m) peak at 3007.05  $\text{cm}^{-1}$  for  $\text{NH}_3^+$  stretching and 1691.66  $\text{cm}^{-1}$  (s) peak.  $\text{NH}_3^+$  deformations observed at 1643.98, 1511.97  $\text{cm}^{-1}$ .  $\text{CO}_2^-$  stretching observed at 1603.19  $\text{cm}^{-1}$ . Peaks of 1249.12, 1153.83  $\text{cm}^{-1}$  confirm presence of higher alkyl group of esters, 755.06  $\text{cm}^{-1}$  for  $(\text{CH}_2)_6$  alkyl chains, C-O and C-C stretching of octanol terminal observed at 989.21  $\text{cm}^{-1}$ . Symmetrical banding vibration of C-H bond of  $\text{CH}_3$  (terminal) confirms 1321.28  $\text{cm}^{-1}$  peak.

**Surface/ interfacial parameters of sodium  $\gamma$ -Octyl aspartate:** Evaluation of surface/ interfacial parameters of surfactant moieties is the most integral and important part of analysis. It provides necessary information about the

surfactant as well as it helps to finalize its various uses. Surface tension at CMC ( $\gamma_{\text{CMC}}$ ), CMC, surface pressure at CMC ( $\pi_{\text{CMC}}$ ), maximum surface excess ( $\Gamma_{\text{max}}$ ) and minimum surface area per surfactant molecule ( $A_{\text{min}}$ ) had been evaluated for this communication. Table 3 shows interfacial parameters for sodium  $\gamma$ -octyl aspartate. Table 4 reports calculated interfacial parameters of binary combinations of SGOA with electrolytes.

**Surface tension at the CMC ( $\gamma_{\text{CMC}}$ ) of sodium  $\gamma$ -Octyl aspartate and its binary combinations:** Table 3 and figure 3 (A) indicate that surface tension at CMC ( $\gamma_{\text{CMC}}$ ) for SGOA was found to be 57.9 dynes/cm.  $\gamma_{\text{CMC}}$  of binary mixtures of SGOA and electrolytes is shown in second column of table 4 and figure 4. Electrolytes are normally added to the surfactant based formulations to enhance their self-life and some other parameters. Therefore, a researcher must know that after addition of an electrolyte, is there any decrease in the surface tension at CMC or not?

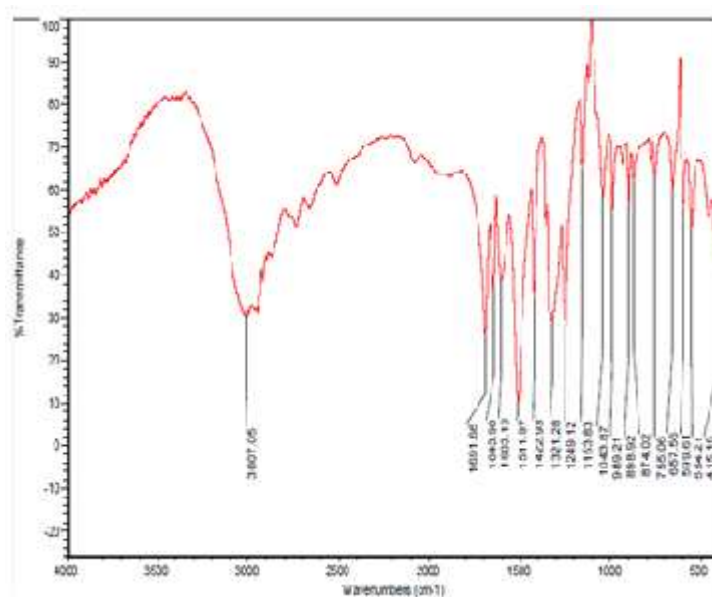
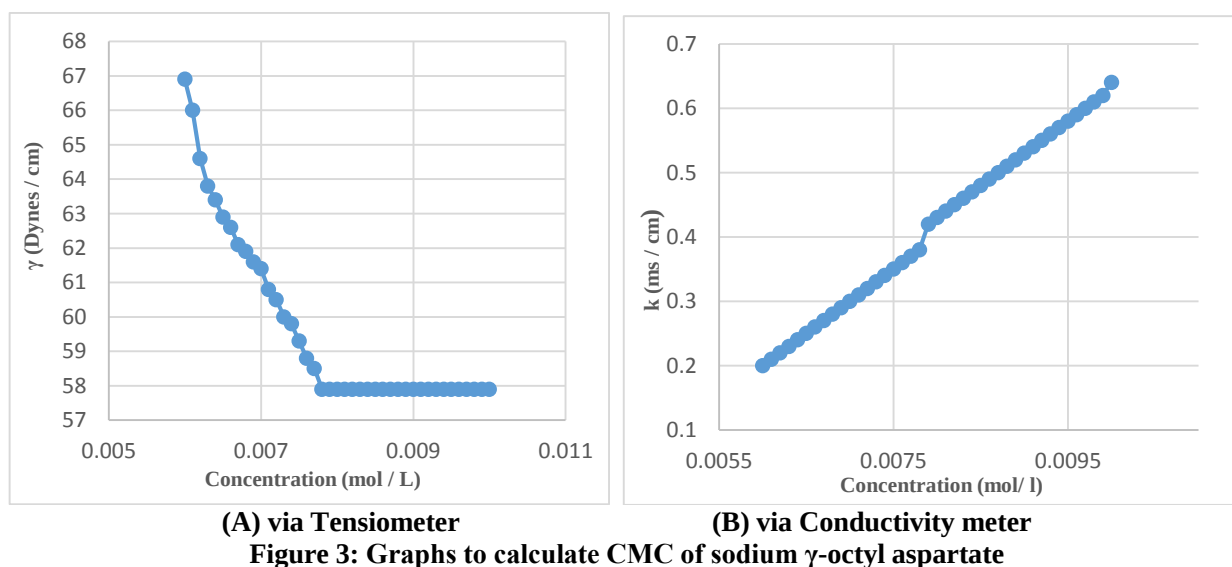


Figure 2: FT-IR spectra of  $\gamma$ -octyl aspartate



The binary mixture of SGOA +  $1 \times 10^{-3}$  M NaCl, shows  $\gamma_{CMC}$  value 56.5 dynes / cm. It clearly indicates the substantial decrease in the  $\gamma_{CMC}$  of binary mixture with respect to pure SGOA (57.9 dynes / cm). When SGOA + KCl was studied, then  $\gamma_{CMC}$  was minutely lower than NaCl case ( $1 \times 10^{-3}$  M) i.e. 56.2 dynes / cm. Little more decrease has been noticed for organic electrolytes. SGOA + NaBenz ( $1 \times 10^{-3}$  M),  $\gamma_{CMC}$  was 55.7 dynes / cm and for NaSaI with same concentration, it was lowest for  $1 \times 10^{-3}$  M and the value is 54.1 dynes / cm. Almost similar pattern for  $\gamma_{CMC}$  was noticed for increase of electrolytes concentration. The value of  $\gamma_{CMC}$  decreases with increase in electrolyte concentration.

#### Change in value of critical micelle concentration (CMC) of SGOA and its mixtures with electrolytes:

Two methods of evaluation of CMC of SGOA and its binary mixtures have been explored: 1) tensiometry and 2) conductivity measurement. All sixteen binary combinations of SGOA with electrolytes were examined to determine CMC; results are reported in third and fourth column of table 4 and data is shown in the form of a graph in figures 5 and 6. CMC evaluation of SGOA is also carried out and data is reported in fourth row of table 3 and figures 3(A) and (B).

In both the methods of evaluation, the difference has been noted hardly at the fourth place of decimal. CMC of pure SGOA was 0.0079 mol/L. On CMC evaluation of binary mixtures, lowest CMC value was noticed for highest concentration of electrolytes. KCl as an electrolyte shows more reduction in CMC values as compared to NaCl. This is due to large atomic radii of  $K^+$  ion with low charge density whereas atomic radii of  $Na^+$  ion are smaller and have high charge density.<sup>32</sup> Furthermore, organic electrolytes show lowest CMC as compared to their inorganic counter parts. The presence of benzene ring in NaBenz and NaSaI imparts hydrophobicity to the mixture, therefore they reduce the CMC further. CMC reduction pattern can be memorized as NaSaI > NaBenz > KCl > NaCl.

**Surface pressure at CMC:** Surface pressure is another foremost parameter to indicate the maximum reduction of surface tension.<sup>25</sup> The surface pressure (effectiveness) at CMC was calculated by the following expression:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (6)$$

where  $\gamma_0$  = Surface tension of distilled water (72 dynes / cm) and  $\gamma_{CMC}$  = Surface tension of  $\gamma$ -octyl aspartate at the CMC.

Table 3

Surface parameters/ thermodynamic properties/ micellization aspects of sodium  $\gamma$ -octyl aspartate (SGOA).

| S.N. | Evaluated parameters                                                        | Obtained value                   |
|------|-----------------------------------------------------------------------------|----------------------------------|
|      | Surface/ Interfacial parameters *                                           |                                  |
| 1.   | Surface tension at CMC ( $\gamma_{CMC}$ )                                   | 57.9 dynes/ cm                   |
| 2.   | Critical micelle concentration (CMC), (by tensiometer)<br>(by conductivity) | 0.0078 mol / L<br>0.0079 mol / L |
| 3.   | Surface pressure at CMC ( $\pi_{CMC}$ )                                     | 14.1 dynes/ cm                   |
| 4.   | Maximum surface excess ( $\Gamma_{max}$ )                                   | $5.63 \mu\text{mol m}^{-2}$      |
| 5.   | Minimum surface area per surfactant molecule ( $A_{min}$ )                  | $29.49 \text{ \AA}^2\text{m}^2$  |
|      | Micellization properties $\Psi$                                             |                                  |
| 6.   | Aggregation number ( $N_{agg}$ )                                            | 34                               |
| 7.   | Pyrene intensity ( $I_1 / I_3$ )                                            | 1.58                             |
| 8.   | Apparent dielectric constant ( $D_{cal}$ )                                  | 46.25                            |
| 9.   | Micelle radius (r)                                                          | 1.40 nm                          |
| 10.  | Surface area per head group ( $a_0$ )                                       | $0.75 \text{ nm}^2$              |
| 11.  | Packing parameter (P)/ Shape of micelle                                     | 0.28/ Spherical                  |
|      | Thermodynamics properties*                                                  |                                  |
| 12.  | Degree of counter-ion dissociation ( $\alpha$ )                             | 0.86                             |
| 13.  | Degree of counter ion binding ( $\beta$ )                                   | 0.14                             |
| 14.  | Standard Free energy ( $\Delta G^0_M$ )                                     | -16.20 kJ/mol                    |
| 15.  | Energy associated with surface contribution ( $\Delta G^0_S$ )              | 2.27 kJ/mol                      |
| 16.  | Hydrophobic free energy ( $\Delta G^0_{HP}$ )                               | -18.47 kJ/mol                    |
| 17.  | Standard free energy of adsorption ( $\Delta G^0_{ads}$ )                   | -18.70 kJ/mol                    |
|      | Biodegradability                                                            |                                  |
| 18.  | Biological oxygen demand (BOD)                                              | 211.2 mg / L                     |
| 19.  | Theoretical oxygen demand (ThOD)                                            | 2.22 gm/ gm                      |
| 20.  | Biodegradation (BOD/ ThOD) (%)                                              | 95.1                             |

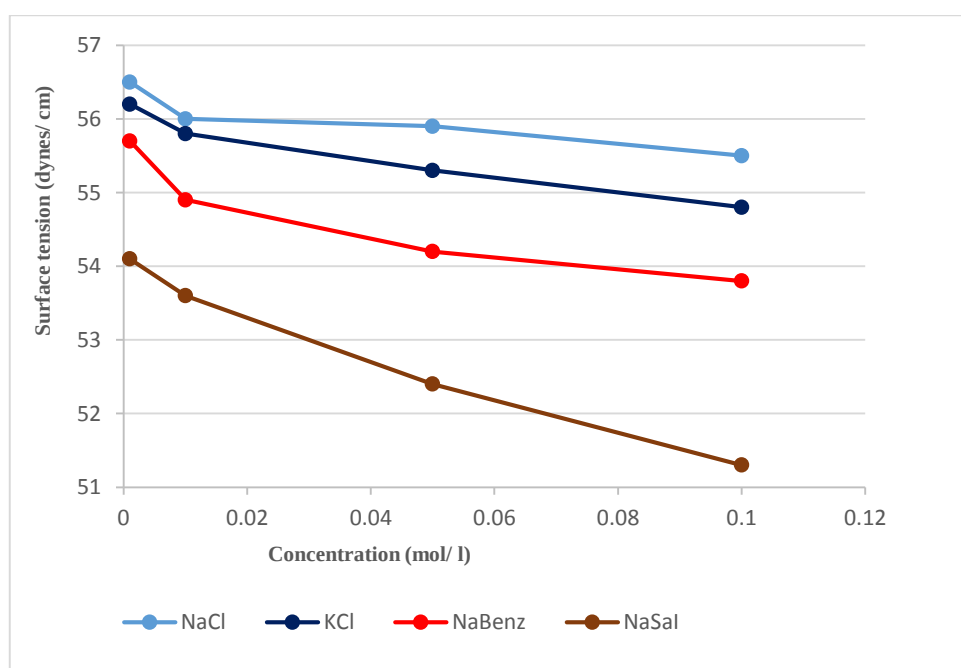
\*The concentration of SGOA for these parameters was  $1 \times 10^{-2}$  M

$\Psi$ For evaluation of micellization parameters, SGOA ( $3 \times \text{CMC}$ ) was used

**Table 4**  
**Evaluated surface parameters of binary mixture of SGOA with inorganic& organic electrolytes.**

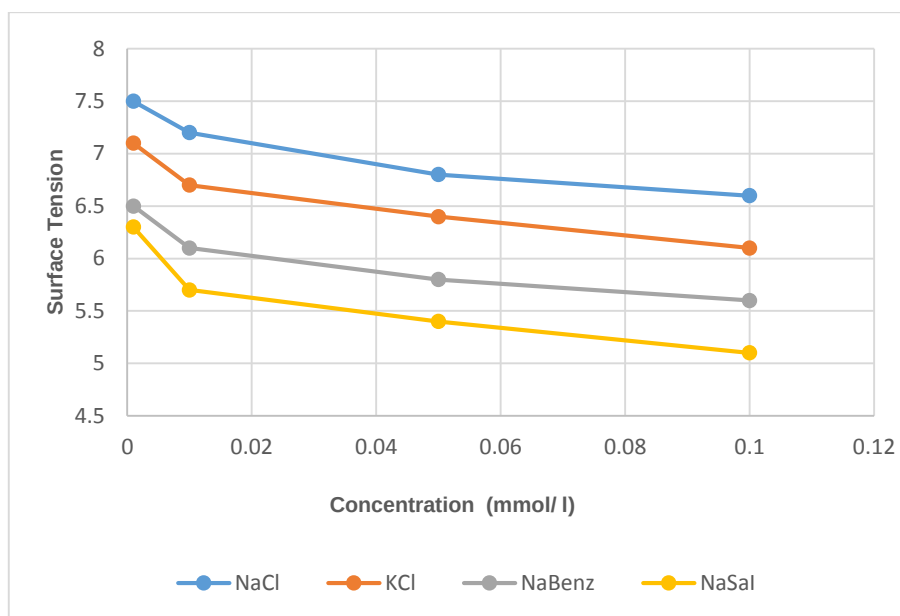
| S.N.           | Binary mixtures                                           | Surface tension at CMC( $\gamma_{\text{CMC}}$ ) [dynes/cm] | Critical micelle concentration (CMC) [ mol/ L] |              | Surface pressure at CMC ( $\pi_{\text{CMC}}$ ) [dynes/cm] | Maximum surface excess ( $\Gamma_{\text{max}}$ ) [ $\mu\text{mol m}^{-2}$ ] | Minimum surface area per surfactant molecules ( $A_{\text{min}}$ ) [ $\text{\AA}^2\text{m}^2$ ] |
|----------------|-----------------------------------------------------------|------------------------------------------------------------|------------------------------------------------|--------------|-----------------------------------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
|                |                                                           |                                                            | Tensiometer                                    | Conductivity |                                                           |                                                                             |                                                                                                 |
| SGOA* + NaCl   |                                                           |                                                            |                                                |              |                                                           |                                                                             |                                                                                                 |
| 1.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-3} \text{ M}$ | 56.5                                                       | 0.0075                                         | 0.0074       | 15.5                                                      | 5.12                                                                        | 32.41                                                                                           |
| 2.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-2} \text{ M}$ | 56.0                                                       | 0.0072                                         | 0.0072       | 16.0                                                      | 5.14                                                                        | 32.32                                                                                           |
| 3.             | $1 \times 10^{-2} \text{ M} + 5 \times 10^{-2} \text{ M}$ | 55.9                                                       | 0.0068                                         | 0.0069       | 16.1                                                      | 5.97                                                                        | 27.83                                                                                           |
| 4.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-1} \text{ M}$ | 55.5                                                       | 0.0066                                         | 0.0065       | 16.5                                                      | 6.43                                                                        | 25.83                                                                                           |
| SGOA* + KCl    |                                                           |                                                            |                                                |              |                                                           |                                                                             |                                                                                                 |
| 5.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-3} \text{ M}$ | 56.2                                                       | 0.0071                                         | 0.0072       | 15.8                                                      | 5.19                                                                        | 31.97                                                                                           |
| 6.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-2} \text{ M}$ | 55.8                                                       | 0.0067                                         | 0.0068       | 16.2                                                      | 5.45                                                                        | 30.47                                                                                           |
| 7.             | $1 \times 10^{-2} \text{ M} + 5 \times 10^{-2} \text{ M}$ | 55.3                                                       | 0.0064                                         | 0.0063       | 16.7                                                      | 5.88                                                                        | 28.24                                                                                           |
| 8.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-1} \text{ M}$ | 54.8                                                       | 0.0061                                         | 0.0061       | 17.2                                                      | 6.24                                                                        | 26.61                                                                                           |
| SGOA* + NaBenz |                                                           |                                                            |                                                |              |                                                           |                                                                             |                                                                                                 |
| 9.             | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-3} \text{ M}$ | 55.7                                                       | 0.0065                                         | 0.0065       | 16.3                                                      | 6.01                                                                        | 27.64                                                                                           |
| 10.            | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-2} \text{ M}$ | 54.9                                                       | 0.0061                                         | 0.0062       | 17.1                                                      | 6.29                                                                        | 26.40                                                                                           |
| 11.            | $1 \times 10^{-2} \text{ M} + 5 \times 10^{-2} \text{ M}$ | 54.2                                                       | 0.0058                                         | 0.0058       | 17.8                                                      | 6.66                                                                        | 24.94                                                                                           |
| 12.            | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-1} \text{ M}$ | 53.8                                                       | 0.0056                                         | 0.0054       | 18.2                                                      | 7.11                                                                        | 23.34                                                                                           |
| SGOA* + NaSal  |                                                           |                                                            |                                                |              |                                                           |                                                                             |                                                                                                 |
| 13.            | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-3} \text{ M}$ | 54.1                                                       | 0.0063                                         | 0.0064       | 17.9                                                      | 6.51                                                                        | 25.51                                                                                           |
| 14.            | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-2} \text{ M}$ | 53.6                                                       | 0.0057                                         | 0.0056       | 18.4                                                      | 6.98                                                                        | 23.80                                                                                           |
| 15.            | $1 \times 10^{-2} \text{ M} + 5 \times 10^{-2} \text{ M}$ | 52.4                                                       | 0.0054                                         | 0.0054       | 19.6                                                      | 7.32                                                                        | 22.69                                                                                           |
| 16.            | $1 \times 10^{-2} \text{ M} + 1 \times 10^{-1} \text{ M}$ | 51.3                                                       | 0.0051                                         | 0.0052       | 20.7                                                      | 7.76                                                                        | 21.41                                                                                           |

\*The concentration of SGOA was  $1 \times 10^{-2} \text{ M}$  for the parameters shown in this Table



**Figure 4: Surface tension at CMC of binary mixture of sodium  $\gamma$ -octyl aspartate with different concentrations of inorganic and organic salts**





**Figure 5: CMC of binary mixture of sodium  $\gamma$ -octyl aspartate with various concentrations of inorganic and organic salts by Du Nouy Tensiometer.**

The surface pressure of sodium  $\gamma$ -octyl aspartate was observed as 14.1 dynes/cm shown in table 3. Surface pressure at CMC for all sixteen salt combinations was calculated and shown in fifth column of table 4.

**Maximum surface excess:** The maximum surface excess is defined as the saturation concentration of surfactant.  $\Gamma_{\max}$  is an important parameter to determine the effectiveness of adsorption of the surfactant at the air-water interface.<sup>11,22</sup> The maximum surface excess of sodium  $\gamma$ -octyl aspartate was calculated by Gibbs adsorption equation:

$$\Gamma_{\max} = \left( -\frac{1}{2.303 nRT} \right) \left( \frac{dy}{d \log C} \right) \quad (7)$$

where  $dy/d \log C$  = slop of the  $\gamma$  versus  $\log C$  at 25°C, R = Gas constant, 8.314 J/mol K, T = Absolute temperature and n = Number of the species at the interface, here n=2.

The maximum surface excess of sodium  $\gamma$ -octyl aspartate was observed 5.63  $\mu\text{mol m}^{-2}$ . Maximum surface excess ( $\Gamma_{\max}$ ) of all sixteen binary combination of SGOA with inorganic and organic electrolytes had been calculated and had been reported in sixth column of table 4. Table 4 revealed that higher concentration of electrolytes increases the  $\Gamma_{\max}$  values. Highest  $\Gamma_{\max}$  values are noted for  $1 \times 10^{-3}\text{M}$  concentration of electrolytes.

**Minimum surface area per surfactant molecules:** Minimum surface area per surfactant molecules indicates the packing degree of surfactant molecule at the air-water interface.<sup>22</sup> The minimum area per molecule of sodium  $\gamma$ -octyl aspartate at the interface was calculated from the following Gibbs adsorption equation:

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \quad (8)$$

where  $N_A$  = Avogadro's number and  $\Gamma_{\max}$  = Maximum surface excess.  $A_{\min}$  value of sodium  $\gamma$ -octyl aspartate was observed 29.49  $\text{\AA}^2\text{m}^2$ . The  $A_{\min}$  depends upon the maximum surface excess of surfactant or its binary solution. The value of  $A_{\min}$  decreased with increased maximum surface excess; values are shown in table 4.

#### **Determination of micellization parameter of (3×CMC) SGOA and its binary combination with electrolytes:**

Steady state fluorescence quenching technique was used to determine all essential micellization parameters of surfactant and its mixtures. The evaluated parameters are aggregation number ( $N_{\text{agg}}$ ), pyrene intensity ( $I_1/I_3$ ), apparent dielectric constant ( $D_{\text{exp}}$ ), micelles radius (r), surface area per head group ( $a_0$ ), packing parameter and shape of micelle. Micellization parameters of SGOA are reported in table 3 whereas in all studied binary mixtures, the concentration of SGOA was 3×CMC along with different concentrations of electrolytes as reported in table 5.

**Micelle's aggregation number:** Aggregation number of micelle indicates that how many monomeric surfactant moieties are found in one micelle of particular surfactant or their mixtures. Steady state fluorescence quenching technique is considered to be an ideal method for determination of aggregation number<sup>4,24</sup>. The aggregation number ( $N_{\text{agg}}$ ) of SGOA is 34 reported in table 3 and figure 7. The perusal of data of column two from table 5, indicates that aggregation number increased on increase of electrolytes concentration for all four studied electrolytes. Highest aggregation number was noticed for SGOA +  $1 \times 10^{-1}\text{M}$  NaCl mixture i.e. 190 whereas lowest was found for SGOA +  $1 \times 10^{-3}\text{M}$  NaSal i.e. 36.

**Pyrene intensity or Micropolarity:** Pyrene intensity or micropolarity<sup>26</sup> of surfactant is ideally calculated by the ratio



of first and third vibronic peaks,  $I_1/I_3$  of fluorescence spectra of compound are given as per equation 9.

$$\text{Pyrene Intensity} = \frac{I_1}{I_3} \quad (9)$$

where  $I_1$  = First vibronic peak of fluorescence spectra and  $I_3$  = Third vibronic peak of fluorescence spectra.

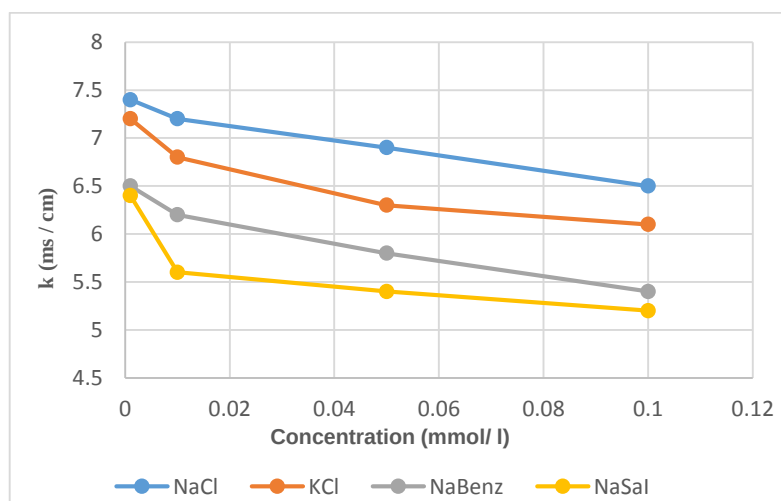
Figure 8 shows the fluorescence spectra of SGOA and  $I_1, I_3$  values are also indicated. All these spectra are used to calculate pyrene intensity of binary combinations and results are reported in third column of table 5.

Micropolarity basically provides information about interaction between surfactant and additives (here it is electrolytes).

**Table 5**  
**Determined micellization parameters of binary mixture of SGOA with electrolytes.**

| S.N.                                   | Binary Mixture               | Aggregation number ( $N_{agg}$ ) | Pyrene intensity ( $I_1/I_3$ ) | Apparent dielectric constant ( $D_{cal}$ ) | Micelle radius (r) [nm] | Surface area per head group ( $a_0$ ) [nm <sup>2</sup> ] | Packing parameter (P) | Shape of micelles |
|----------------------------------------|------------------------------|----------------------------------|--------------------------------|--------------------------------------------|-------------------------|----------------------------------------------------------|-----------------------|-------------------|
| <b>SGOA <math>\Psi</math> + NaCl</b>   |                              |                                  |                                |                                            |                         |                                                          |                       |                   |
| 1.                                     | 3×CMC + $1 \times 10^{-3}$ M | 40                               | 1.62                           | 49.44                                      | 1.48                    | 0.71                                                     | 0.30                  | Spherical         |
| 2.                                     | 3×CMC + $1 \times 10^{-2}$ M | 46                               | 1.60                           | 47.85                                      | 1.55                    | 0.68                                                     | 0.31                  | Spherical         |
| 3.                                     | 3×CMC + $5 \times 10^{-2}$ M | 100                              | 1.59                           | 47.05                                      | 2.02                    | 0.52                                                     | 0.40                  | Cylindrical       |
| 4.                                     | 3×CMC + $1 \times 10^{-1}$ M | 190                              | 1.54                           | 43.06                                      | 2.49                    | 0.42                                                     | 0.50                  | Cylindrical       |
| <b>SGOA <math>\Psi</math> + KCl</b>    |                              |                                  |                                |                                            |                         |                                                          |                       |                   |
| 5                                      | 3×CMC + $1 \times 10^{-3}$ M | 41                               | 1.62                           | 49.44                                      | 1.50                    | 0.70                                                     | 0.30                  | Spherical         |
| 6.                                     | 3×CMC + $1 \times 10^{-2}$ M | 62                               | 1.56                           | 44.66                                      | 1.73                    | 0.61                                                     | 0.34                  | Cylindrical       |
| 7.                                     | 3×CMC + $5 \times 10^{-2}$ M | 97                               | 1.53                           | 42.26                                      | 1.99                    | 0.52                                                     | 0.40                  | Cylindrical       |
| 8.                                     | 3×CMC + $1 \times 10^{-1}$ M | 144                              | 1.54                           | 43.06                                      | 2.27                    | 0.46                                                     | 0.46                  | Cylindrical       |
| <b>SGOA <math>\Psi</math> + NaBenz</b> |                              |                                  |                                |                                            |                         |                                                          |                       |                   |
| 9.                                     | 3×CMC + $1 \times 10^{-3}$ M | 38                               | 1.63                           | 50.24                                      | 1.69                    | 0.95                                                     | 0.22                  | Spherical         |
| 10                                     | 3×CMC + $1 \times 10^{-2}$ M | 46                               | 1.56                           | 44.66                                      | 1.80                    | 0.90                                                     | 0.23                  | Spherical         |
| 11.                                    | 3×CMC + $5 \times 10^{-2}$ M | 98                               | 1.49                           | 39.07                                      | 2.31                    | 0.70                                                     | 0.30                  | Spherical         |
| 12.                                    | 3×CMC + $1 \times 10^{-1}$ M | 140                              | 1.59                           | 47.05                                      | 2.60                    | 0.62                                                     | 0.34                  | Cylindrical       |
| <b>SGOA <math>\Psi</math> + NaSal</b>  |                              |                                  |                                |                                            |                         |                                                          |                       |                   |
| 13.                                    | 3×CMC + $1 \times 10^{-3}$ M | 36                               | 1.06                           | 47.52                                      | 1.65                    | 0.98                                                     | 0.21                  | Spherical         |
| 14.                                    | 3×CMC + $1 \times 10^{-2}$ M | 50                               | 0.53                           | -37.55                                     | 1.84                    | 0.88                                                     | 0.24                  | Spherical         |
| 15.                                    | 3×CMC + $5 \times 10^{-2}$ M | 87                               | 0.52                           | -38.34                                     | 2.22                    | 0.73                                                     | 0.29                  | Spherical         |
| 16.                                    | 3×CMC + $1 \times 10^{-1}$ M | 143                              | 0.51                           | -39.14                                     | 2.61                    | 0.62                                                     | 0.35                  | Cylindrical       |

$\Psi$  Here (3×CMC) SGOA solution was used



**Figure 6: CMC of binary mixture of sodium  $\gamma$ -octyl aspartate with different concentrations of inorganic and organic salts by Conductivity Method.**

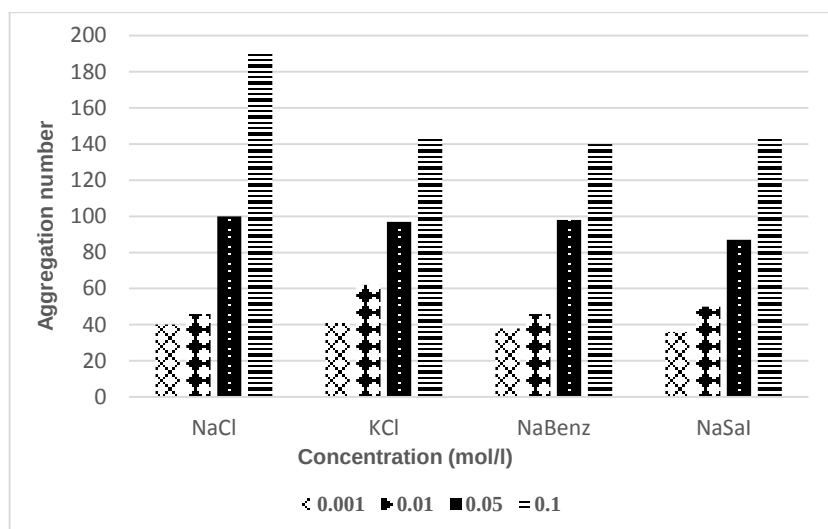


Figure 7: Aggregation number of binary mixture of sodium  $\gamma$ -octyl aspartate with salts.

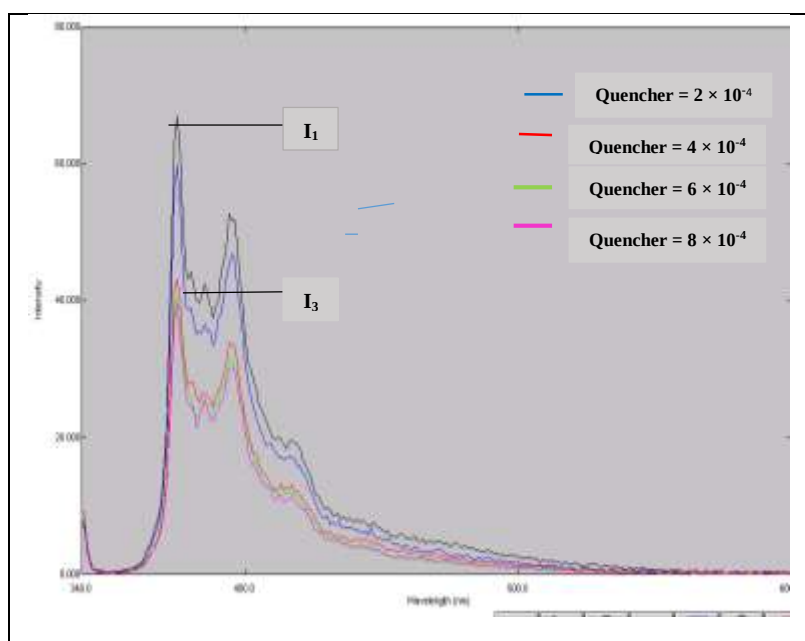


Figure 8: Fluorescence spectra of sodium  $\gamma$ -octyl aspartate indicating intensities of pyrene (probe) and benzophenone (quencher).

Decreasing value of pyrene intensity reveals that there is a strong interaction between surfactant moiety and added electrolytes.<sup>22</sup> Second reason could be that those counter ions are strongly bounded between head groups of surfactant in the stern layer of the electrical double layer surrounding the surfactant head groups.

However, the electrostatic repulsion decreases between head groups and enhances the electrical layer surrounding the ionic group. This kind of internal scenario ultimately reduces the pyrene intensity of binary mixture. Micropolarity (pyrene intensity) of SGOA is 1.58 and it is 1.54 for SGOA +  $1 \times 10^{-1}$  M NaCl. It indicates that higher concentration of NaCl provides good micropolarity. In the case of organic electrolytes, drastic reduction was noticed for all concentrations of NaSal. The lowest micropolarity was 0.51 for SGOA +  $1 \times 10^{-1}$  M.

**Apparent dielectric constant:** Apparent dielectric constant of micellization is calculated for SGOA and for all studied binary combinations by using equation 10:

$$\frac{I_1}{I_3} = 1.000461 + 0.01253 D_{cal} \quad (10)$$

Equation 10 shows that  $D_{exp}$  totally depends on the micropolarity.<sup>2</sup> The  $D_{cal}$  of SGOA was 46.25 as reported in table 3. The  $D_{cal}$  values of all studied binary mixtures are shown in fourth column of table 5.

Binary mixture of SGOA +  $1 \times 10^{-1}$  M NaCl showed  $D_{exp}$  value 43.06 lowest one at high concentration of NaCl. But with KCl as electrolyte, lowest  $D_{cal}$  is 42.26 for SGOA +  $5 \times 10^{-2}$  M KCl. The  $D_{cal}$  39.07 was calculated for SGOA +  $5 \times 10^{-2}$  M NaBenz binary mixtures. When NaSal was used as

an electrolyte, then lowest  $D_{cal}$  values were reported and it was -39.14 for SGOA +  $1 \times 10^{-1}$  M NaSal.

**Micelle's radius:** Micelle radius of pure surfactant or mixture of surfactant ( $r$ , nm) was calculated by using following equation:<sup>5</sup>

$$r = \left[ \frac{3vN_{agg}}{4\pi} \right]^{1/3} \quad (11)$$

where  $v$  = volume of the hydrophobic chains of  $\gamma$ -octyl aspartate and  $N_{agg}$  = aggregation number of surfactant and its binary mixture.

Volume of the hydrophobic chains of surfactant was calculated by equation 12:<sup>30</sup>

$$v = (27.4 + 26.9 n_c) \times 10^{-3} \text{ nm}^3 \quad (12)$$

where  $n_c$  = Total number of carbon atom used in specific calculation.

The volume of SGOA was found to be  $0.3502 \text{ nm}^3$  as  $n_c$  was 12 (total number of C atom in SGOA). For binary mixture of SGOA with NaCl and KCl,  $n_c$  was 12 (as NaCl and KCl do not have any carbon) whereas, in case of, NaBenz and NaSal, presence of phenyl group of benzoate and salicylate ion had been taken for account. Volume of binary mixture of SGOA + NaBenz and SGOA + NaSal was found to be  $0.5385 \text{ nm}^3$ , as  $n_c$  was 19, twelve carbon from SGOA and seven carbon benzene ring.

Micelle radius ( $r$ ) of SGOA was  $1.40 \text{ nm}$  as reported in table 3. Micelle radii of all binary combinations of SGOA are shown in fifth column of table 5. All four electrolytes have shown increase in the radii of mixed micelles with increase in electrolytes concentration. Large radii were noticed at maximum concentration of all electrolytes i.e.  $1 \times 10^{-1}$  M. Largest radii of mixed micelle were calculated for SGOA +  $1 \times 10^{-1}$  M NaSal mixture i.e.  $2.61 \text{ nm}$ .

**Surface area per head group:** Surface area per head group ( $a_0$ ,  $\text{nm}^2$ ) was calculated as per equation 13:<sup>5</sup>

$$a = \frac{3v}{r} \quad (13)$$

where  $v$  = Volume of the hydrophobic chains of  $\gamma$ -octyl aspartate and  $r$  = Micelle radius.

Surface area per head group for SGOA is  $0.75 \text{ nm}^2$  shown in table 3,  $a_0$  is calculated for all sixteen studied binary combinations and reported in sixth column of table 5. The lowest surface area per head group was calculated as  $0.42 \text{ nm}^2$  for SGOA +  $1 \times 10^{-1}$  M NaCl mixed solution.

**Packing parameter and shape of micelle:** Packing parameter<sup>7,10,13</sup> ( $P$ ) is an important parameter to understand various properties of surfactant and its binary mixture viz.

viscosity, capacity to solubilize in water-insoluble material and cloud point. The value of packing parameter decides the shape of micelle (surfactant alone or binary mixtures).

Israelachvili et al<sup>9</sup> gave expression to calculate the packing parameter,  $P$  of micelle of surfactant or mixed micelle.

$$P = \frac{v}{a_0 l} \quad (14)$$

where  $v$  = volume of the hydrophobic chains of  $\gamma$ -octyl aspartate,  $a_0$  = surface area per head group and  $l$  = length of hydrophobic chains of surfactant / mixed solution.

Equation 15 was used to calculate length of surfactant / mixed surfactant.<sup>30</sup>

$$l = (1.5 + 1.265 n_c) \times 10^{-1} \text{ nm} \quad (15)$$

where  $n_c$  is same as mentioned for equation 12.

Length of SGOA was found to be  $1.668 \text{ nm}$  and this is used for calculation of packing parameter of all binary mixture of SGOA with NaCl and KCl. Length of SGOA and NaBenz and NaSal was calculated,  $2.554 \text{ nm}$  and was used to calculate packing parameter of all SGOA + NaBenz solution and SGOA + NaSal.

The shape of micelle depends upon numerical value of packing parameter. The packing parameter value is  $P < 1/3$  (spherical shape),  $1/3 < P < 1/2$  (cylinder shape),  $1/2 < P < 1$  (vesicles or bilayer shape) and  $P > 1$  (reverse micelle structure).<sup>13</sup>

Packing parameter was found to be  $0.28$  for SGOA alone and micelle would be spherical reported in table 3. Packing parameter ( $P$ ) and shape of mixed micelle (binary mixture micelle) are reported in seventh and eighth columns of table 5. When highest concentration  $10^{-1}$  M of all four studied electrolytes was investigated, then the shape of mixed micelle was found to be cylindrical. But, when lowest concentration ( $1 \times 10^{-3}$ ) of electrolytes was studied, then spherical shaped mixed micelle was observed in all four used electrolytes.

**Thermodynamic parameters of SGOA and its binary mixtures:** Thermodynamic studies of surfactant alone and with additives are evaluated to understand the interaction between surfactant-surfactant, surfactant-additives and additives-additives. Thermodynamic studies also revealed various energies associated with these interactions. Degree of counter-ion dissociation ( $\alpha$ ), degree of counter-ion binding ( $\beta$ ), standard free energy ( $\Delta G^0_M$ ) and energy associated with surface contribution ( $\Delta G^0_s$ ), hydrophobic free energy ( $\Delta G^0_{HP}$ ) and standard free energy of adsorption ( $\Delta G^0_{ads}$ ) were calculated for SGOA and values are reported in table 3. All above mentioned thermodynamic parameters were also calculated for all sixteen binary mixture of SGOA

with NaCl, KCl, NaBenz and NaSal and evaluated values are reported in table 6.

**Degree of counter-ion dissociation and counter-ion binding:** The degree of the counter-ion dissociation ( $\alpha$ ) of SGOA and all binary combinations is obtained by the conductivity method. The degree of the counter-ion dissociation ( $\alpha$ ) was determined by plotting a graph between conductivity (k) versus concentration of surfactant/concentration of the binary mixture.

The expression used to calculate the degree of counter-ion dissociation<sup>7, 13</sup> is:

$$\alpha = \frac{S_2}{S_1} \quad (16)$$

where  $S_1$  = pre micellar region and  $S_2$  = post micellar region.

The degree of counter-ion binding of SGOA alone and its binary mixtures were calculated by the equation 17:

$$\beta = 1 - \frac{S_2}{S_1} \quad (17)$$

where  $S_1$  and  $S_2$  were mentioned in expression (16).

The slope ratio was calculated from figure 3 (B). Degree of the counter-ion dissociation ( $\alpha$ ) of SGOA was calculated to be 0.86 and  $\beta$  would be 0.14 as reported in table 3. Concentration of binary mixture versus conductivity (k) has been plotted for all sixteen binary mixtures but not shown in the communication. All calculations were carried out by those graphs and calculated values are reported in second and third column of table 6. The highest degree of counter-ion dissociation was calculated for SGOA +  $1 \times 10^{-3}$  M KCl,  $\alpha$  is 0.93 whereas smallest  $\alpha$  was found for SGOA +  $1 \times 10^{-1}$  M NaSal i.e. 0.67. This could be due to aromatic salicylate ion which does not enhance the disassociation of NaSal.

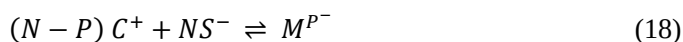
**Table 6**  
Calculated thermodynamic parameters of binary mixture of SGOA with used electrolytes.

| S.N.                  | Binary Mixture                              | The degree of counter-ion dissociation ( $\alpha$ ) | The degree of counter-ion binding ( $\beta$ ) | Standard Free energy ( $\Delta G^0_M$ ) [kJ/mol] | Energy associated with surface contribution ( $\Delta G^0_s$ ) [kJ/mol] | Hydrophobic free energy ( $\Delta G^0_{HP}$ ) [kJ/mol] | Standard free energy of adsorption ( $\Delta G^0_{ads}$ ) [kJ/mol] |
|-----------------------|---------------------------------------------|-----------------------------------------------------|-----------------------------------------------|--------------------------------------------------|-------------------------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------------------|
| <b>SGOA* + NaCl</b>   |                                             |                                                     |                                               |                                                  |                                                                         |                                                        |                                                                    |
| 1.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-3}$ M | 0.88                                                | 0.12                                          | -16.38                                           | 1.96                                                                    | -18.34                                                 | -19.41                                                             |
| 2                     | $1 \times 10^{-2}$ M + $1 \times 10^{-2}$ M | 0.86                                                | 0.14                                          | -16.45                                           | 2.30                                                                    | -18.75                                                 | -19.56                                                             |
| 3.                    | $1 \times 10^{-2}$ M + $5 \times 10^{-2}$ M | 0.82                                                | 0.18                                          | -16.55                                           | 2.98                                                                    | -19.53                                                 | -19.25                                                             |
| 4.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-1}$ M | 0.75                                                | 0.25                                          | -16.70                                           | 4.17                                                                    | -20.87                                                 | -19.27                                                             |
| <b>SGOA* + KCl</b>    |                                             |                                                     |                                               |                                                  |                                                                         |                                                        |                                                                    |
| 5.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-3}$ M | 0.93                                                | 0.07                                          | -16.45                                           | 1.15                                                                    | -17.60                                                 | -19.49                                                             |
| 6.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-2}$ M | 0.91                                                | 0.09                                          | -16.57                                           | 1.49                                                                    | -18.07                                                 | -19.54                                                             |
| 7.                    | $1 \times 10^{-2}$ M + $5 \times 10^{-2}$ M | 0.81                                                | 0.19                                          | -16.77                                           | 3.19                                                                    | -19.96                                                 | -19.60                                                             |
| 8.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-1}$ M | 0.78                                                | 0.22                                          | -16.85                                           | 3.71                                                                    | -20.55                                                 | -19.61                                                             |
| <b>SGOA* + NaBenz</b> |                                             |                                                     |                                               |                                                  |                                                                         |                                                        |                                                                    |
| 9.                    | $1 \times 10^{-2}$ M + $1 \times 10^{-3}$ M | 0.89                                                | 0.11                                          | -16.70                                           | 1.84                                                                    | -18.53                                                 | -19.41                                                             |
| 10.                   | $1 \times 10^{-2}$ M + $1 \times 10^{-2}$ M | 0.81                                                | 0.19                                          | -16.82                                           | 3.20                                                                    | -20.02                                                 | -19.54                                                             |
| 11.                   | $1 \times 10^{-2}$ M + $5 \times 10^{-2}$ M | 0.78                                                | 0.22                                          | -16.97                                           | 3.73                                                                    | -20.07                                                 | -19.64                                                             |
| 12.                   | $1 \times 10^{-2}$ M + $1 \times 10^{-1}$ M | 0.77                                                | 0.23                                          | -17.17                                           | 3.95                                                                    | -21.12                                                 | -19.73                                                             |
| <b>SGOA* + NaSal</b>  |                                             |                                                     |                                               |                                                  |                                                                         |                                                        |                                                                    |
| 13.                   | $1 \times 10^{-2}$ M + $1 \times 10^{-3}$ M | 0.88                                                | 0.12                                          | -16.75                                           | 2.01                                                                    | -18.76                                                 | -19.50                                                             |
| 14.                   | $1 \times 10^{-2}$ M + $1 \times 10^{-2}$ M | 0.85                                                | 0.15                                          | -17.07                                           | 2.56                                                                    | -19.63                                                 | -19.71                                                             |
| 15.                   | $1 \times 10^{-2}$ M + $5 \times 10^{-2}$ M | 0.82                                                | 0.18                                          | -17.17                                           | 3.90                                                                    | -20.26                                                 | -19.85                                                             |
| 16.                   | $1 \times 10^{-2}$ M + $1 \times 10^{-1}$ M | 0.67                                                | 0.33                                          | -17.24                                           | 5.69                                                                    | -22.93                                                 | -19.91                                                             |

\*The concentration of SGOA was  $1 \times 10^{-2}$  M for the parameters shown in this Table

**Standard free energy of micelle:** A mass action model is a parameter for the analysis of the interaction between synthesized SGOA + additives, SGOA + SGOA. The mass action model is based upon the dissociation-association equilibrium between surfactant, monomers and micelles present in solution.<sup>13,31</sup>

The equilibrium interaction between counter-ions  $C^+$ , surfactant monomers  $S^-$  and mono-dispersed micelles  $M^P$  can be signified as follows:



Thus, the equilibrium constant for equation 18 can be related to the standard free energy of micelle formation per monomer unit by:

$$\frac{\Delta G_M^0}{RT} = -\left(\frac{1}{N}\right) \ln C_{M^{P-}} + \ln C_{S^-} + \left(1 - \frac{P}{N}\right) \ln C_{C^+} \quad (19)$$

The standard free energy per surfactant molecules ( $\Delta G_M^0$ ) associated with forming the micelle is given by equation 19.

$$\Delta G_M^0 = RT \ln X_{CMC} \quad (20)$$

Further, when additives are mixed with surfactant, then  $\Delta G_M^0$  consists of the interaction SGOA - SGOA, SGOA-additives and additives-additives. The energy associated with these interactions consists of three types of contribution shown in equation 21.<sup>16,31</sup>

$$\Delta G_M^0 = \Delta G_{HP}^0 + \Delta G_{el}^0 + \Delta G_{all\ other}^0 \quad (21)$$

where  $\Delta G_{HP}^0$  = hydrophobic free energy associated with transferring the surfactant hydrocarbon chain from the medium into the interior of the micelle,  $\Delta G_{el}^0$  = Association with the electrostatic interactions between heads groups of surfactants and counter-ions and  $\Delta G_{all\ other}^0$  = All other contribution energy of the specific interaction during micellization.<sup>3</sup>

$\Delta G_M^0$  of SGOA alone was calculated -16.20 kJ/mol. The value ( $\Delta G_M^0$ ) was calculated for all SGOA + electrolytes and reported in column four of table 6. Concentration  $1 \times 10^{-3}$  M was mixed with SGOA, then there was not a very substantial decrease noticed with respect to SGOA  $\Delta G_M^0$  value.  $\Delta G_M^0$  for SGOA +  $1 \times 10^{-3}$  M NaCl, KCl, NaBenz and NaSal was calculated and found as -16.38, -16.45, -16.70 and -16.75 kJ/mol.

**Energy association with surface contribution:** In equation 21,  $\Delta G_{el}^0$  and  $\Delta G_{all\ other}^0$  are two vital energies of micellization to form a yield of energy associated with surface contributions as equation 22.<sup>3,16</sup>

$$\Delta G_S^0 = \Delta G_{el}^0 + \Delta G_{all\ other}^0 \quad (22)$$

Further,  $\Delta G_S^0$  can be calculated by using equation 23:

$$\Delta G_S^0 = -\beta RT \ln X_{CMC} \quad (23)$$

where  $\beta$  = Degree of the counter-ion binding, R = Universal gas constant, T = Absolute temperature and  $X_{CMC}$  = CMC value in mole fraction.

$\Delta G_S^0$  for pure SGOA was found to be 2.27 kJ/mol and reported in table 3. For all binary combinations of SGOA,  $\Delta G_S^0$  values are reported in the fifth column of table 6. SGOA +  $1 \times 10^{-3}$  M KCl showed a substantial decrease i.e. 1.15 kJ/mol. When individual column is analysed from top to bottom, an increase in the concentration of electrolyte enhanced the value of  $\Delta G_S^0$  substantially for all studied combinations.

**Hydrophobic free energy:** The hydrophobic free energy ( $\Delta G_{HP}^0$ ) is an important thermodynamic parameter to understand the complete micellization process. The general equation is used to express  $\Delta G_{HP}^0$  value by equation 24. Further equation 24 is also useful to evaluate  $\Delta G_{HP}^0$ .

$$\Delta G_{HP}^0 = RT \ln X_{CMC} + RT \left(1 - \frac{P}{N}\right) \ln X_{CMC} \quad (24)$$

where P/N = Degree of counter-ion dissociation ( $\alpha$ ) and  $X_{CMC}$  = Mole fraction of the surfactant at CMC.

In aqueous solution, CMC value is underneath  $10^{-1}$  M, then equation 24, can be re-written as:<sup>3,16</sup>

$$\Delta G_{HP}^0 = RT \ln X_{CMC} + RT \left(1 - \frac{P}{N}\right) \ln \left(\frac{CMC}{w}\right) \quad (25)$$

where w = molarity of the water.

$\Delta G_{HP}^0$  value of SGOA was determined -18.47 kJ/mol and reported in table 3.  $\Delta G_{HP}^0$  values of all studied sixteen binary combinations were explored and shown in sixth column of table 6. Here, an interesting pattern has been noticed that inorganic electrolytes are having lowest concentration, then further increased with respect to pure SGOA. Organic anionic terminations having electrolytes have shown further decrease in the  $\Delta G_{HP}^0$  value; -18.53 kJ/mol was found for SGOA  $\times 10^{-3}$  M NaBenz and 18.76 kJ/mol for SGOA  $\times 10^{-3}$  M NaSal.

**Standard free energy of adsorption:** Standard free energy of adsorption<sup>6</sup> of synthesized surfactant/binary mixture at the air-water interface was calculated by the following equation:

$$\Delta G_{ads}^0 = \Delta G_M^0 - \frac{\pi_{CMC}}{\Gamma_{max}} \quad (26)$$

where  $\Delta G_M^0$  = Standard free energy of the micelle,  $\pi_{CMC}$  = Surface pressure and  $\Gamma_{max}$  = Maximum surface excess concentration.

$\Delta G_{ads}^0$  value for pure SGOA was -18.70 kJ/mol as reported in table 3. To maintain the symmetry of the work, this

thermodynamic parameter was evaluated for all sixteen binary combinations of SGOA with all four studied electrolytes and values are reported in the last column of table 6. Here, data of  $\Delta G_{\text{ads}}^0$  indicate that similar value was calculated for  $\text{SGOA} \times 10^{-3} \text{ M NaCl}$  and  $\text{SGOA} \times 10^{-3} \text{ M NaBenz}$  i.e. -19.41 kJ/mol. The maximum decrease in the value of  $\Delta G_{\text{ads}}^0$  was for  $\text{SGOA} \times 10^{-1} \text{ M NaSal}$  i.e. -19.91 kJ/mol.

**Biological oxygen demand:** For evaluation of biodegradability of any compound, it is biological oxygen demand (BOD) on 0<sup>th</sup> day and 7<sup>th</sup> day has to be calculated as a standard procedure in Winkler's method. Authors have strictly followed all strength of the chemicals meticulously as given in standard procedure of Winkler's and BOD was found 211.2 mg / L.

**Theoretical oxygen demand (ThOD):** Theoretical oxygen demand of  $\gamma$ -octyl aspartate was calculated as per reaction (2 and 3).<sup>27</sup> The ThOD was calculated 2.22 gm / gm and finally, biodegradation was found to be 95.1 %.

## Conclusion

Present communication revealed that  $\gamma$ -octyl aspartate (amino acid-based surfactant) may have 46.2 % yield if the duration of esterification is 24 hours, molar ratio of reactant 1: 1.00 and temperature of the esterification kept 65 °C. All evaluated surface/ interfacial parameters, thermodynamic properties and micellization aspects as well as its biodegradation of SGOA, show that it is a promising surfactant for its individual use and the formulation based on it. Surface/ interfacial parameters of binary mixtures of SGOA and NaCl, KCl, NaBenz and NaSal showed that lower concentrations of electrolytes are good enough to have all desired values to make SGOA based commercial product. When NaCl and KCl were used as electrolytes, then KCl proved to be a better electrolyte as compared to NaCl. NaBenz and NaSal are having organic anionic moiety, benzoate ion in the case of NaBenz and salicylate ion in the case of NaSal. NaSal looked to be on the higher side to all evaluated surface parameters.

Various evaluated micellization properties showed almost similar kind of pattern of used electrolytes as it was noticed in interfacial parameters evaluation. Lower concentration of all electrolytes with SGOA formed a spherical micelle whereas highest concentration of electrolytes showed a cylindrical shape of the micelle. Six studied thermodynamic parameters for pure SGOA and its sixteen binary combinations after evaluation revealed that all parameters are showing good acceptability of SGOA with inorganic and organic electrolytes normally found in various useful formulations. The percent of biodegradation  $\gamma$ -octyl aspartate was calculated 95.1 %.

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