SYNTHESIS AND CHARACTERIZATION OF GEMINI SURFACTANTS – GSI

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Abstract:

Gemini Surfactants the rent generation of surfactants are more efficient in adsorbing at the aq. Solution air interface reducing the surface tension and forming micelles. Here, the Gemini surfactant GSI prepare from stearic and chloride with L-cystine. It is characterized by analytical technique like UV-visible spectrophotometer, DSC, FT-IR Spectrophotometer and Thermal analysis.

Introduction:

The surfactants, i.e., surface active agents have certain characteristic features and mode of action. They are composed of groups with opposing solubility tendencies typically an oil – soluble hydrocarbon chain and a H_2O soluble ionic or polar groups.

Surfactants are soluble in atleast one phase of a liquid system. They absorb at interfaces so that at equllibrium, the concentration of a liquid system i.e., of a surfactant at a phase boundry is greater that its bulk concentration. They form oriented, monolayers at these interfaces. When the surfactant concentration in the bulk solution exceeds a certain value called, the critical micelle concentration or CMC an aggregate called 'Micelle' is formed.

Small amounts of surfactants can have dramatic effects. They can make a surface wettable or water repellent, change the rate of an organic ran by order of magnitude create or break a foam, change the viscosity of a slurry, suspend a solid in H_2O of precipitate.

Organic molecules that possess both hydrophilic and hydrophobic (libpophile) parts have been termed as ampiphiles or surfactants.

The hydrophilic part (head group) is charged either cationic, zwitterionic or anionic or polar (non-ionic). Based on these head group charge, surfactants are divided into 4 categories.

1. Anionic Surfactants.
   Ex:- Sodium dodecyl sulphate (SDS)
2. Cationic Surfactants.
   Ex:- Cetyl trimethyl ammonium bromide (CTAB)
3. Non-ionic Surfactants.
   Ex:- Twin 80, Twin 100
4. Zwitherionic Surfactants.
   Ex:- N-alkyl – N, N-dimethyl betaines, etc.

The lipophillic part (tail group) is usually consists of hydrocarbon chain C_6 to C_{20} normal or branched. The solubility in different medium and micelle forming properties are a net effect of both the head and the tail part of a surfactant.

In 1991, the name Gemini surfactants was assigned by Menger etal. Gemini surfactants are surfactants that have 2 hydrophilic gps and two hydrophobic groups per molecule rather the single hydrophilic and single hydrophobic group of conventional surfactants or in otherwards the amphiphiles possessing a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group and another hydrocarbon tail.

Gemini surfactants with rigid spacer, however might conceivably grow linearly. Another advantage of the Gemini surfactant is, the much lower temperature at which their solubility becomes equal to their CMC and higher

solubilities in water than comparable conventional surfactants. This means greater convenience when Gemini surfactants are used in product formation.

Gemini generally have lower critical micelle concentration (CMC), their forming and wetting properties are excellent, resulting in a more efficient lowering of the surface tension of H2O, they also show unexpected viscosity changes as their concentration is increased.

Such molecular features of surfactants are important for developing new surfactant system for specific applications.

Materials and Methods:

Materials :

1. 1-dodecanoic acid (Stearic acid)
2. Dichloromethane
3. L-cystine

Purification of solvent:

Dichloromethane passed through sodium sulphate to remove moisture before used in the experiment.

Ditilled H2O have been used whenever necessary.

Preparation of GSI

Stearic acid chloride with L-Cystine.

Step 1 *:*

Preparation of stearic acid chloride.

Saturated fatty acid chlorides were prepared using theonyl chloride. A typical procedures was given below.

2g of 1-dodecanic acid (stearic acid) was taken in a clean dried round bottom flask and 20ml of petroleum ether and 1 ml of theonyl chloride were added to it. The whole content was refluxed over water bath to a period of 3 to 4 hrs.

During the reaction, evolved SO2 gas taken care to let out. The Petroleum ether was distilled of under vacuum. The acid chlorides were remaining in the flask. This have been used for further experiment in the preparation of Gemini surfactants.

$CH_3(CH_2)_{16}COOH + SOCl_2 \xrightarrow{\text{(Reflux over 3-4 hrs)}} CH_3(CH_2)_{16}COCl + SO_2 + HCl$

Theonyl chloride — Stearic acid chloride

Step 2 :

Stearic Acid Chloride with L-cystine.

Stearic acid chloride diluted with dichloro methane (DCM) in a 100ml round bottom flask. Finely crushed powered 0.841g L-cystile weighed and added to the acid chloride (without addition of any solvent) followed by vigorous stirring. Stirring carried out for 3-4 days at room temperature.

After it, the solution poured into pure DCM and washed with DCM for 3 to 4 times. Then it was placed in heating water bath (to evaporate the solvent). Dried, light brown colour was obtained.

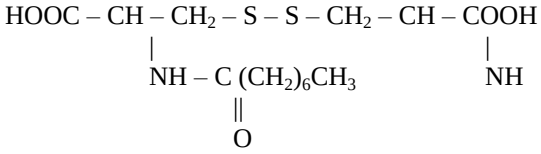
Yield = 80%

Melting point = 53.29°C

$CH_3(CH_2)_{16}COCl + HOOC - CH(NH_2)CH_2 - S - S - CH_2 - CH(NH_2)$

↓ |

COOH



Analytical Methods :

Gemini surfactants were characterized by analytical techniques like UV-visible, FT-IR spectroscopy and differential scanning colorimetric and Thermograuimetric analysis.

FT – IR Spectrotometer :

For the Gemini surfactant, FT – IR spectra have been recorded in the form of KBr pellets to get insight into the $–NH_2$, $-CH_2$, CH_3, – S – S – and – COOH absorption in the surfactants.

Thermal Analysis :

Thermogravimetry analysis and DSC have been carried out to find out the thermal stability and lather property by pupont thermal analysis system.

Differential scanning calorimetry studies (DSC)

All DSC measurements were done on Dupont 2000 Thermal Analyser. The peak areas were estimated by DuPont Advanced general U4.1C programme.

Results and Discussion :

The prepared gemini surfactant is characterized by FT – IR, DSC & TGA.

FT – IR Spectroscopy:

The shape of an absorption band around $3000cm^{-1}$ responsible for –CHgp present in the molecule.

Thermo Gravimetric Analysis :

For the prepared Gemini surfactants characterized by JGA to get insight in thermal stability of the same in the N_2 atmosphere. GSI shows single stage decomposition at weight los 93.11% with onset temp 187°C and final temperature 227°C.

Differential Scanning Colorimetry :

The polymeric states of dimeric surfactants and their lather property by DSC experiment. The surfactants are having 4 polymorphic states i.e. α, β, Δ, Ω.

The lather value of the surfactants evaluated in the following manner.

LV = jlg Ω + j/g (B) / j/g (Ω)

j/g = Integration of peak areas in Joules/gm.

For GSI j/g = 153.5

$\therefore$ The LV of GSI = 1.

Conclusions :

GSI prepared from stearic acid after the conversion to stearic acid chloride and cystenine is diamer as flexible one. the Gemini surfactant have well characterized and confirmed by FT – IR, DSC and TGA. The lathering value of GSI report by using DSC data. i.e. Lt had high lather value.

TABLE

Assignment of the FT – IR Characteristics absorption peaks of GS1

Name of the Gemini Surfactant	Region (cm-1)	Assignment of Peaks
GS 1	3446.80	O – H Str (w)
	2955.22	C – H Str (w)
	2919.37	C – H Str (s)
	2842.56	C – H Str (m)
	1695.53	C – O Str (m)
	1628.96	N – H Str (W)
	1470.22	O – H Str (W)
	1408.77	O – H Str (W)

References :

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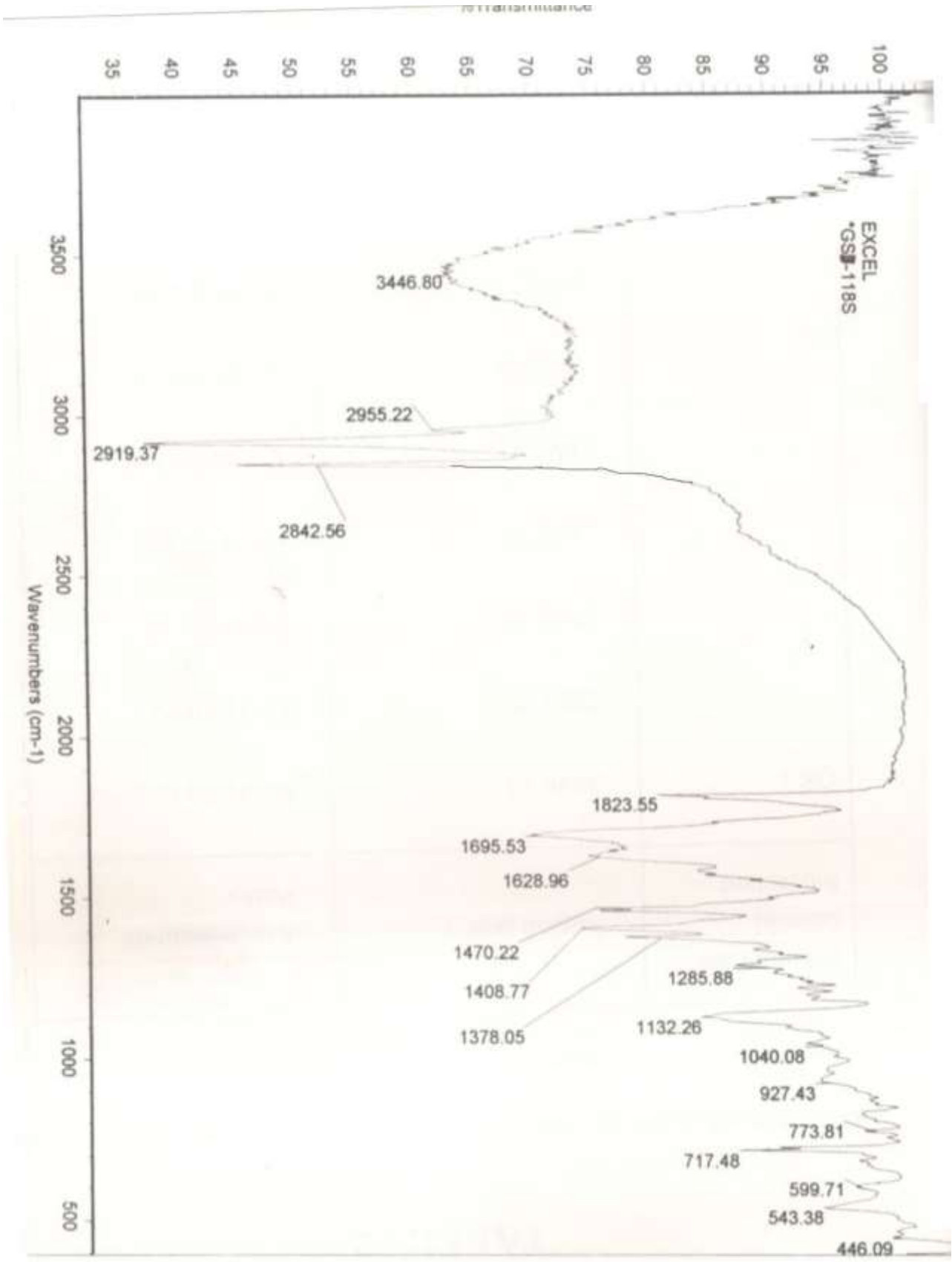
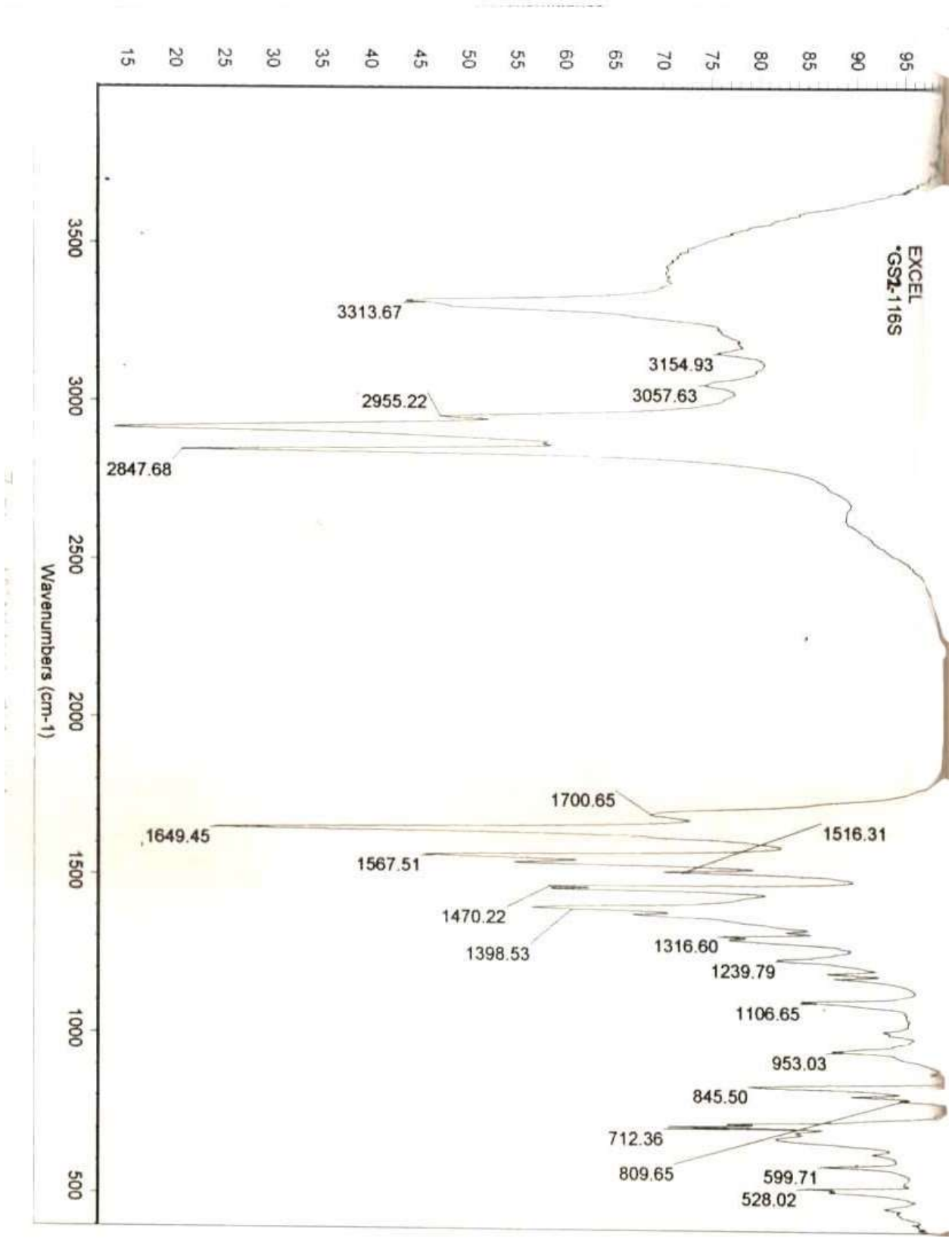
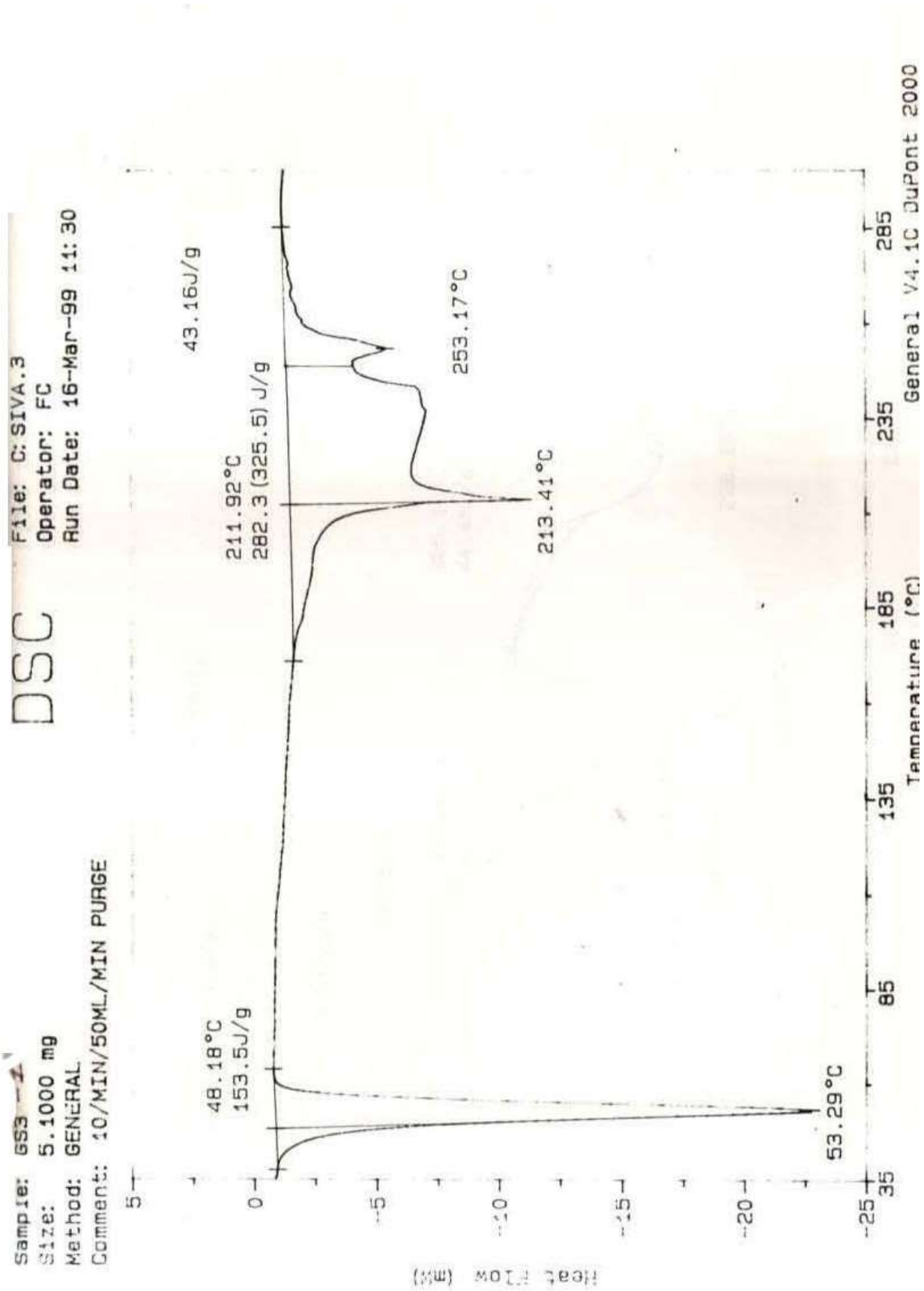
2. Rosen, M.J. Chem Tech 30, 1993.
3. Friberg, S.E. Rudhag L Tenider 7, 2, 1970.
4. Masuyama, A, Kirito, Y.I. Okalara MJAM oil Chem Soc. 68,539.1991.


%Transmittance
35
40
45
50
55
60
65
70
75
80
85
90
95
100
EXCEL
*GS-118S
3446.80
2955.22
2919.37
2842.56
1823.55
1695.53
1628.96
1470.22
1408.77
1378.05
1285.88
1132.26
1040.08
927.43
773.81
717.48
599.71
543.38
446.09
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


EXCEL
*GS2-116S
3313.67
3154.93
3057.63
2955.22
2847.68
1700.65
1649.45
1516.31
1567.51
1470.22
1398.53
1316.60
1239.79
1106.65
953.03
845.50
712.36
809.65
599.71
528.02
Wavenumbers (cm-1)


DSC
File: C:SIVA.3
Operator: FC
Run Date: 16-Mar-99 11:30
Sample: GS3 -1
Size: 5.1000 mg
Method: GENERAL
Comment: 10/MIN/50ML/MIN PURGE
43.16J/g
211.92°C
282.3 (325.5) J/g
253.17°C
213.41°C
48.18°C
153.5J/g
53.29°C
Heat Flow (mW)
Temperature (°C)
General V4.1C DuPont 2000