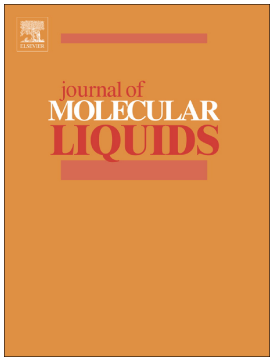

A relative study on the micellization behavior of 12–2–12 Gemini surfactant with lactose and maltodextrin in aqueous medium: Spectroscopic and conductometric analysis

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A relative Study on the Micellization Behavior of 12–2–12 Gemini Surfactant with Lactose and Maltodextrin in Aqueous Medium: Spectroscopic and Conductometric Analysis

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Abstract

The present work reports the micellization mechanism and physico–chemical properties of synthesized 12–2–12 Gemini surfactant in aqueous solution of carbohydrates (lactose and maltodextrin) (0.0, 0.5, 1.0) % (w/v) at varying temperatures in the range (293.15-313.15) K. For this purpose, conductometric as well as spectroscopic measurements have been engaged to analyze the micellar modulation of Gemini surfactant in terms of its critical micelle concentration (*CMC*). The carbohydrates (lactose/maltodextrin) have been found to decrease the *CMC* of 12-2-12 Gemini surfactant, however, the effect is much more pronounced in maltodextrin as compared to lactose which is in compliance with the hydrophobic region present in the molecules. Further, temperature dependence of *CMC* has been employed to compute thermodynamic parameters of micellization in order to procure a better knowledge about the behavior of surfactant and intermolecular interactions present in such systems. The study of aqueous Gemini–carbohydrate systems may be helpful in working towards a healthier world from both personal as well as environmental aspects of life.

Keywords: Conductivity; Critical micelle concentration; 12–2–12 Gemini surfactant; thermodynamics of micellization; spectroscopic technique.

1. Introduction

Surfactants (surface active agents) are imperative components in biological systems as well as pharmaceutical processes, thereby, account for large consumption in industrial and commercial applications [3-6]. Their biocompatible, biodegradable and non-toxic formulations have greater potential in food preparation and processing [7-8]. In recent years, a new class of surfactants called Gemini surfactants emerged as promising substitutes for conventional surfactants [9-12]. They have superiority in terms of surface activity i.e aggregation behavior (micellization), solubility and efficiency in lowering interfacial tension [13]. These in turn, lead to recurrent appearance of surfactants in diverse fields ranging from routine commercial products to the high technology products thereby motivating us to pursue their synthesis and study their aggregation behavior in aqueous solution. The interactions of surfactants (conventional or Gemini) with carbohydrates account for the structural organization of bio–active molecules in living systems and is a subject matter of extensive research in the field of material synthesis, green chemistry, chemical engineering, biochemistry (gene therapy) etc. [1, 2].

The micellization process and micro-environment of surfactants are largely affected by the presence of additives such as carbohydrates, amino acids, drugs, electrolytes, etc. as well as with change in experimental conditions [14-17]. Surfactants have the ability to modify the conformation of carbohydrates in aqueous solutions, thereby, lead to the change in the appearance, functionality, stability or rheology of the solution. Range of possible functional modifications depends upon the nature of surfactant-additive interactions, which might favor or counter the self-association process and consequently, influence the micellar morphology and its environment [18-21]. Therefore, it would be beneficial to study the micellization behavior of Gemini surfactants in the presence of biologically important compounds like carbohydrates, which can promote our understanding about the interaction mechanism of Gemini–aqueous carbohydrate system. In addition, this may encourage the scientific community towards the development of materials with improved functional attributes or bulk physico–chemical properties.

Thus, in the present work, we have studied the aggregation modulation of synthesized cationic 12–2–12 Gemini surfactant i.e. ethanediyl–1,2–bis(dimethyldodecylammonium bromide) in aqueous solutions of carbohydrates (lactose and maltodextrin) by making use of electrical conductometry. The thermodynamic parameters have been calculated and analyzed to get better understanding of unique behavior of Gemini surfactants in aqueous medium of

carbohydrates and their chemical–biological relationships. Additive (carbohydrate) association with surfactant has also been monitored spectrophotometrically by employing fluorescence and UV–visible spectrophotometric techniques. For conductivity measurements, a spectrum of temperature ranging from 293.15 K to 313.15 K at a regular interval of 5 K has been selected to study the temperature dependence as well. However, the spectroscopic studies have been carried out at room temperature (i.e. 298.15 K).

2. Experimental

2.1 Materials

Double distilled water with conductivity of ~2–3×10^{-6} S·cm^{-1} and pH of ~6.8 –7.0 (at 298.15 K) obtained from Millipore distillation unit was used for all the studies. Gemini surfactant i.e. ethanediyl–1,2–bis(dimethyldodecylammonium bromide) was synthesized in the laboratory using ethyl acetate, 1-bromododecane and N, N, N, N–tetramethyl ethylenediamine (TEMED) which were obtained from Merck, Sisco Research Laboratory and Himedia respectively. Maltodextrin from the Loba Chemie Pvt. Ltd. and α –Lactose monohydrate from SD Fine–Chem. Ltd. Both Carbohydrates were recrystallized twice in distilled water and dried in vacuum oven for 24 hrs at ~ 50–60^{o}C [22]. Pyrene of purity > 96% obtained from Merck was used as spectrophotometric probe. The provenance and purity of chemicals used have also been provided in Table 1.

Table 1: Specification of Chemicals Used.

Chemical Name	Source	Purification method	Mass Fraction Purity[a]
ethyl acetate ($C_4H_8O_2$)	Merck	–	0.99
1-bromododecane	Sisco Research Laboratory	–	0.98
N,N,N,N–tetramethyl ethylenediamine (TEMED) ($C_6H_{16}N_2$)	Himedia	–	0.99
Maltodextrin	Loba Chemie Pvt. Ltd.	Recrystallisation	0.98
Lactose ($C_{12}H_{22}O_{11}\cdot H_2O$)	SD Fine–Chem. Ltd.	Recrystallisation	0.95
Pyrene($C_{16}H_{10}$)	Merck	–	0.96

[a]Declared by Supplier

2.2 Instrumentation

The following instruments have been used for characterization and to procure information on micellization behavior of synthesized 12–2–12 Gemini surfactant in aqueous solution of carbohydrates (lactose and maltodextrin).

2.2.1 Characterization of 12–2–12 Gemini surfactant:

- ^{1}H and ^{13}C NMR analysis were carried out in D_2O solvent using JNM–ECS400 spectrometer with field strength 400 MHz.
- The IR spectrum was obtained from RZX (Perkin Elmer) Fourier Transform Spectrometer (FTIR) at room temperature in the range of 4000–400 cm^{-1}.

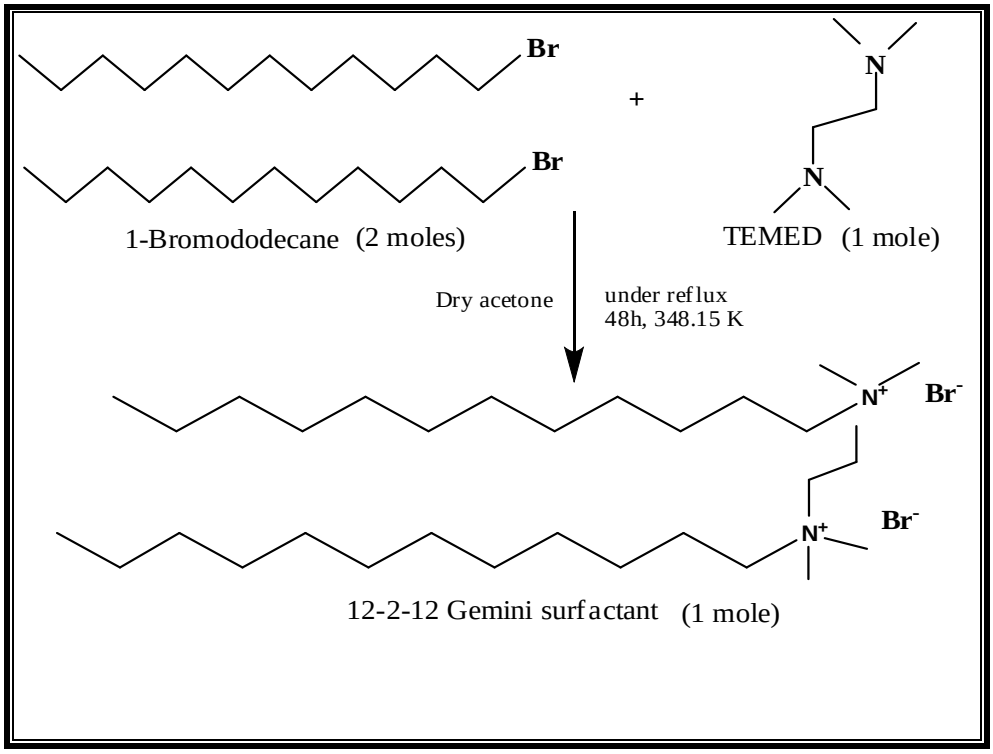
2.2.2. Micellization Behavior of Synthesized 12–2–12 Gemini Surfactant:

- Digital conductivity meter (Cyberscan Con–510) has been employed for conductivity measurements.
- Perkin Elmer LS–55 Fluorescence Spectrophotometer has been used for the fluorescence probe study.
- Genesys 10S UV–Vis spectrophotometer (190–900 nm) supplied by Thermo Scientific USA, has been used for obtaining UV visible absorption spectrum.

2.3 Synthesis of 12–2–12 Gemini Surfactant

Gemini surfactant i.e. ethanediyl–1,2–bis(dimethyldodecylammonium bromide) was prepared by following the well established procedure (**Scheme 1**) reported in literature [23,24]. Mixture of N, N, N, N–tetramethyl ethylene diamine (TEMED) and 1–bromododecane (molar ratio of 1:2) in 10 ml of ethyl alcohol was taken in round bottom flask then 5 ml of acetone was added to remove turbidity and get clear solution. This solution was then refluxed at 348.15 K for approximately 48 hours until the entire volume of TEMED was consumed. After removal of the solvent by evaporation, the prepared waxy compound was allowed to cool at room temperature

and washed with mixture of ethyl acetate and acetone in 1:1 ratio. The washing was repeated 6–7 times to eliminate excess of alkyl bromide. The resulting white product was crystallized twice in dry acetone and dried in vacuum oven at 323.15 K.



Scheme 1: Systematic scheme for the synthesis of 12–2–12 Gemini surfactant

2.4 Methods

2.4.1 Conductivity Measurements

Stock solution of carbohydrates (0.0, 0.5, 1.0) % (w/v) have been prepared in water and has been used as solvent for the preparation of 12–2–12 Gemini surfactant of different concentrations (0.076–1.458 mmol·kg^{-1}). All the solutions have been prepared by using Shimadzu balance with a precision 0f ±0.0001g. The working principle of conductivity meter has already been discussed in our earlier publication [3]. However, the conductivity cell has been calibrated before each measurement by using conductivity standard calibration solution with conductivity 84 and 1413×10^{-6} S·cm^{-1} supplied by Eutech instruments. The temperature of the solution was maintained to ± 0.1 K by circulating water through the vessel containing the solution with the help of a high power digital water circulator supplied by Riviera Pvt. Ltd. Mumbai. The

conductivity, κ for 12–2–12 Gemini surfactant in aqueous solutions of lactose/maltodextrin with percentage composition (0.0, 0.5, and 1.0) % (w/v) have been measured in temperature range (293.15–313.15) K at an interval of 5 K.

2.4.2 Spectroscopic Measurements

Fluorescence probe study has been carried out at room temperature (298.15 K) keeping the excitation wavelength at 334 nm and recording emission at 373 nm and 384 nm in the wavelength range (350-450) nm. The working principle of the instrument and the method for the preparation of Pyrene solution of required concentration has been explained elsewhere [3]. The excitation and emission slit widths were kept at 8 nm and 2.5 nm respectively. The absorption spectra have been recorded in (200-400) nm wavelength range and at room temperature (298.15 K) from UV–Vis spectrophotometer using 10 mm path length quartz cuvette.

3. Result and Discussion

3.1 Chemical Structure

The analysis of ^{1}H NMR, ^{13}C NMR and FTIR spectra of synthesized 12–2–12 Gemini surfactant confirms its chemical structure.

3.1.1 ^{1}H NMR

The ^{1}H NMR spectrum (**Fig. 1**) of 12–2–12 Gemini surfactant shows resonance at δ 0.84–0.88 ppm (t, 6H, alkyl chain, 2 × 1 CH_3), 4.79 ppm (s, 4 H, spacer, 1× N^+ CH_2CH_2 N^+), 3.30 ppm (s, 12H, 2×2 N^+ CH_3), 1.31–1.81 ppm (m, 4H, 2× CH_2 attached to each terminal C), 3.53–3.55 ppm (m, 4 α H, alkyl chain, 2× N^+–CH_2) and 1.81–2.93 ppm (m, 36 H, alkyl chain, 9× 2 CH_2).

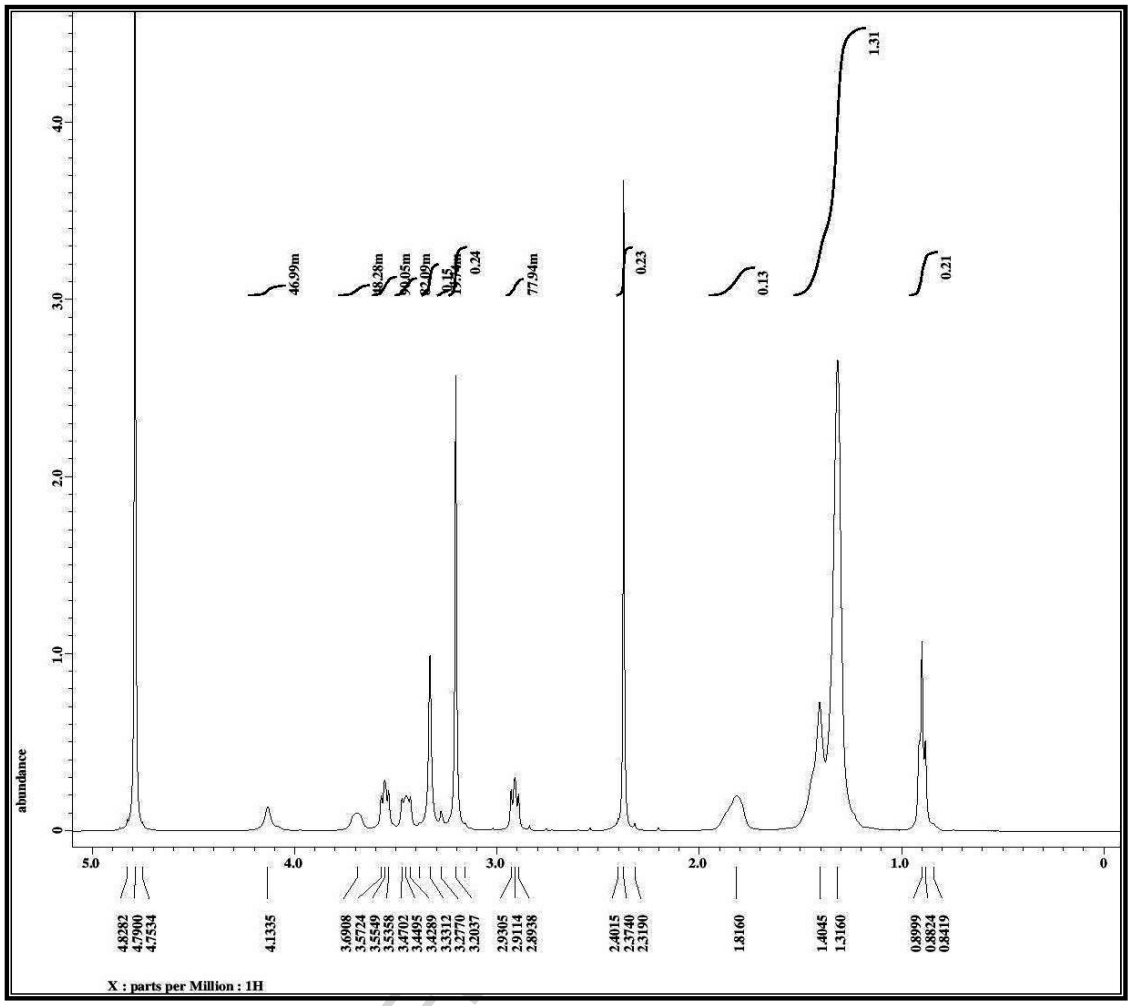


Fig. 1: ^{1}H–NMR spectrum of 12–2–12 Gemini surfactant

3.1.2 C^{13} NMR

The ^{13}C NMR spectrum of synthesized 12–2–12 Gemini surfactant is shown in **Fig. 2**.The resonance at δ–64.32 ppm (C–atom of –CH_2 group as spacer), 63.28 ppm (α –C of –CH_2 group of the alkyl chain length), 13.9 ppm (C–atom of terminal –CH_3 groups of hydrophobic tail), 60.18, 52.71, 44.69, 32.00, 30.16, 29.88, 29.83, 29.72, 29.52, 22.69 (10 C–atoms of –CH_2 group of alkyl chain).The two C–atoms of –CH_3 groups directly attached to N–atom are expected to give same chemical shift but they resonate at δ – 51.48 ppm and 51.29 ppm. The small difference in these values may be due to some rotation in the molecule which makes the two carbon atoms to reside in different environments..

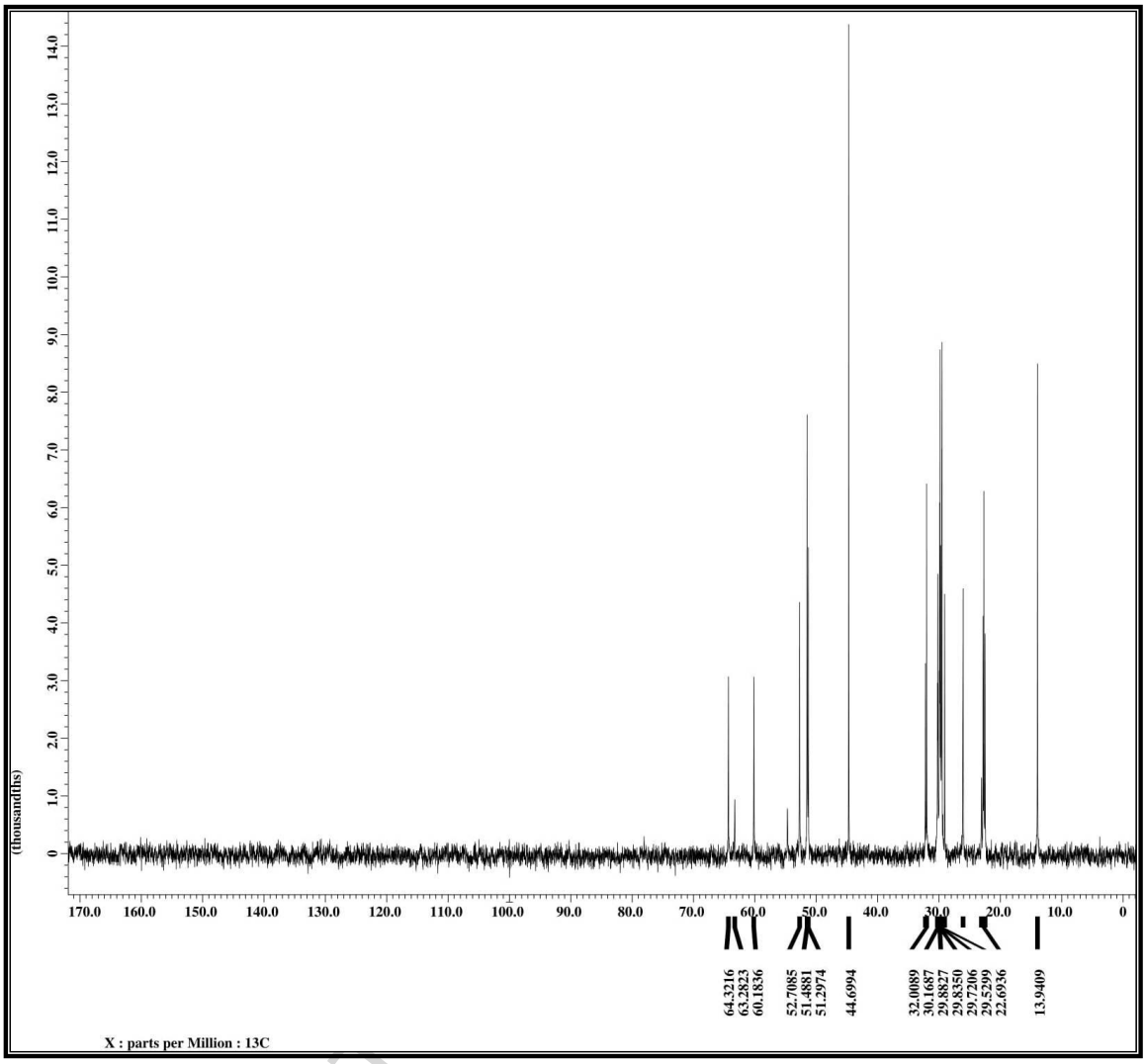


Fig. 2: ^{13}C–NMR spectrum of 12–2–12 Gemini surfactant

3.1.3 FTIR Spectrum

The spectrum of pure 12–2–12 Gemini surfactant (**Fig. 3**) showing peaks at 2858 cm^{-1} and 2959 cm^{-1} (symmetric and asymmetric stretching, methylene group of alkyl chain), 1465 cm^{-1} (scissoring, C–H bending), 1380 cm^{-1} (bending, $–CH_3$ groups which is attached directly to the nitrogen), 2780 cm^{-1} (stretching, –CH of terminal $–CH_3$ group), 1160 cm^{-1} and 978 cm^{-1} (stretching, $C–N^+$), 2925 cm^{-1} (asymmetric stretching, methylene group of spacer) and 720 cm^{-1} (rocking, $–CH_2$ bending).

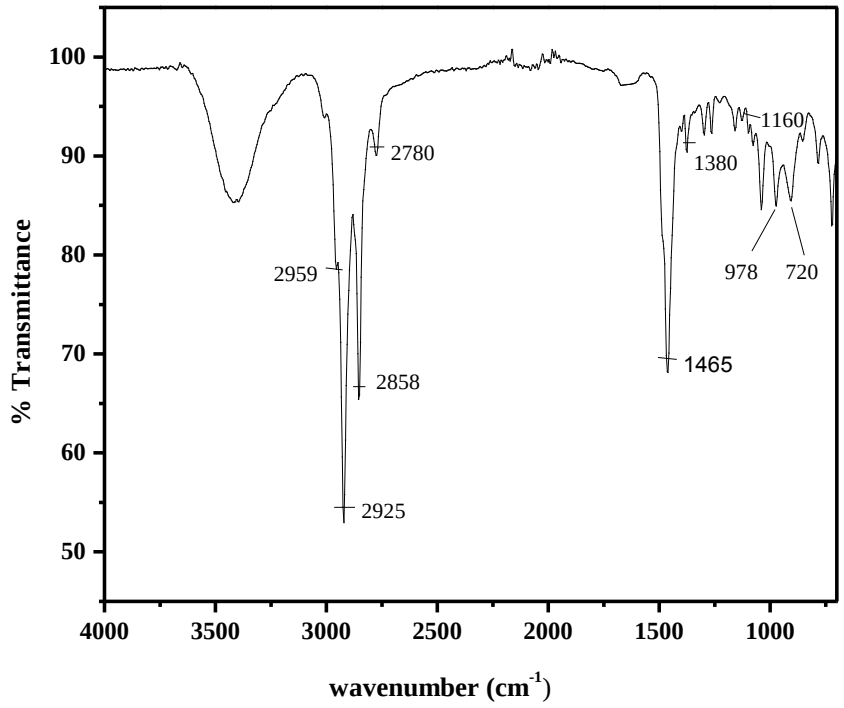


Fig. 3: Infrared spectrum of 12–2–12 Gemini surfactant

3.2 Critical Micelle Concentration (CMC) Determination

3.2.1 Conductivity Measurements

The Conductivity values of 12–2–12 Gemini surfactant in (0.0, 0.5, 1.0) % (w/v) lactose/maltodextrin have been shown in Table S1 and S2 of supplementary data. In each experimental set, κ varies linearly with [Gemini surfactant] in pre–micellar and post–micellar region, the intersection of the slopes corresponds to a particular point, referred to as critical micelle concentration (*CMC*). The conductivity values have been found to increase sharply before *CMC* but, vary slowly after *CMC* . At low concentration, mobility plays an important role as ions are relatively far apart and therefore have larger contribution towards κ (sharp increase) , but at higher concentrations, presence of micelles inhibit the movement of ionic species as a result conductivity increases slowly [25].

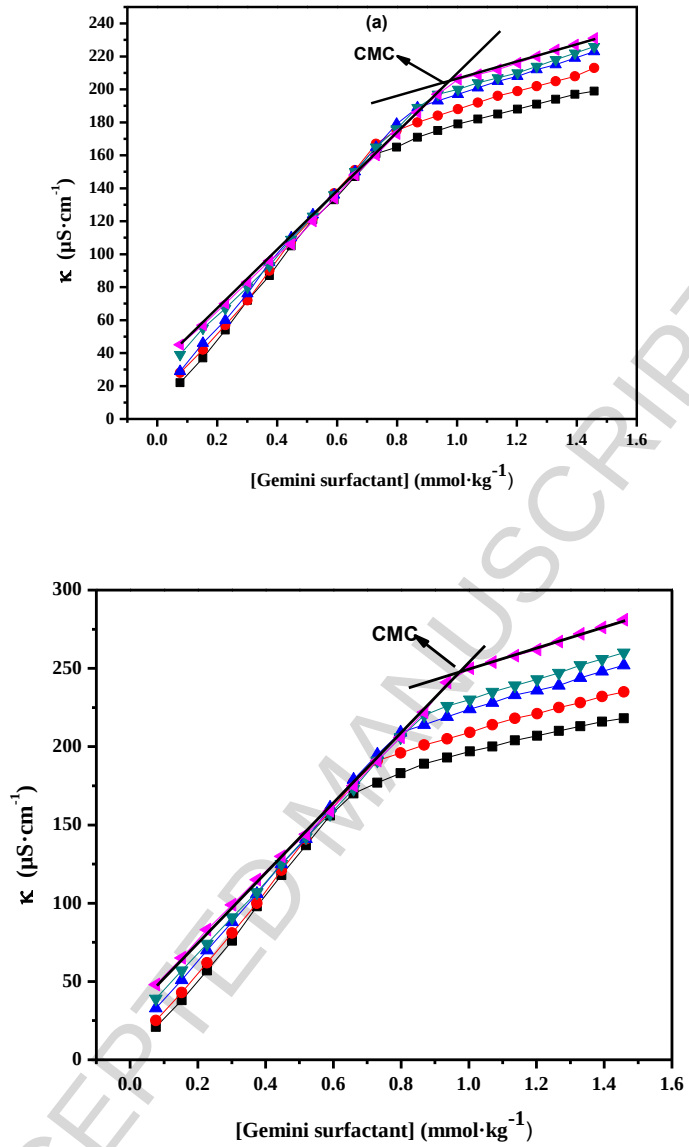


Fig. 4: Representative plots of κ, versus [Gemini surfactant] in 1.0 % (w/v) aqueous solution of (a) Lactose and (b) Maltodextrin at 293.15 K (■), 298.15 K (●), 303.15 K (▲), 308.15 K (▼), and 313.15 K (◄).

The conductivity values of 12–2–12 Gemini surfactant in pure water (electrolyte) are higher in comparison to the aqueous solutions of carbohydrates (non electrolytes). Comparatively, the κ values of lactose are lower than that of maltodextrin, as it, being smaller molecule, is largely hydrated which leads to the inhibition in movement of species. The *CMC* values of 12-2-12 Gemini surfactant in aqueous solutions of lactose and maltodextrin are documented in Table 2 and the values follow the order: no additive > lactose > maltodextrin. It has been assumed that

in the presence of carbohydrates, water–water interactions are replaced by water–sugar interactions cause the dehydration of hydrophilic group and results in decrease in *CMC*. Moreover, carbohydrates have the tendency to promote the formation of water matrix which lower degree of hydrophilic hydration reinforcing the micellization and thus lowers the *CMC* values [26-28].

Table 2: *CMC* of 12–2–12 Gemini surfactant in aqueous solutions of lactose and maltodextrin (m^a = 0.0, 0.5 and 1.0% (w/v)) at different temperatures (T/K).

T (K)	*CMC* $\cdot 10^3$ (mol·kg^{-1})				
	Lactose			Maltodextrin	
	^{a}m (0.0%)	^{a}m (0.5%)	^{a}m (1.0%)	^{a}m (0.5%)	^{a}m (1.0%)
293.15	0.80	0.75	0.72	0.69	0.66
	0.85 (0.88)[a]	0.81	0.78	0.76	0.72
298.15	(0.86)[c]	(0.80)[c]	(0.78)[c]	(0.77)[c]	(0.74)[c]
	(0.85)[d]	(0.81)[d]	(0.79)[d]	(0.77)[d]	(0.73)[d]
303.15	0.92(0.95)[b]	0.87	0.85	0.84	0.81
308.15	0.99	0.96	0.90	0.90	0.88
313.15	1.06 (1.11)[b]	1.02	0.98	0.99	0.97

^{a}m is the percentage of lactose and maltodextrin(w/v) in water. Standard uncertainties, u, are u(T) = 0.01 K and u(*CMC*) = $0.01 \cdot 10^{-3}$ mol·kg^{-1}, (level of confidence = 0.68).

[a] Ref 30 [b] Ref 29 [c] Fluorescence study [d] UV–Visible study.

3.2.2 Fluoroscence Pyrene Probe Measurements

Fluorescence probe technique is one of the powerful tools in investigating the association of surfactant in the presence of carbohydrates. In order to determine the *CMC* values of 12–2–12 Gemini surfactant in aqueous solutions of lactose/maltodextrin with percentage composition (0.0, 0.5, and 1.0) % (w/v) at room temperature, we have amplified the pyrene probe fluorescence spectra for aqueous 12–2–12 Gemini surfactant.

Pyrene has been used as a probe in this study and there were five emission peaks at 373, 379, 383, 389 and 393 nm for pyrene (2×10^{-6} mol·kg^{-1}) fluorescence spectra [31,32]. Pyrene

fluorescence spectrum depends on the vibronic fine structure and relative peak intensity is strongly dependent on the microenvironment polarity. The polarity–induced changes in photophysical properties of pyrene can be determined by measuring the ratio of emission intensities between first and third bands (I_1/I_3) [32]. Lower value of I_1/I_3 indicates apolar environment and vice varsa [33]. With increasing polarity, the intensity of first band is increased (I_1) but on the other hand, there is no effect on the intensity of third band (I_3) [34]. Since pyrene, being hydrophobic molecule, has a much lower aqueous solubility (about 10^{-7} mol·kg^{-1}) than in hydrophobic solvent (0.075 mol·kg^{-1}), it is very strongly distributed into micelles as soon as they form, and the transfer is accompanied by abrupt decrease in the I_1/I_3 ratio indicating micelle formation (apolar environment), when a surfactant is added to aqueous solution containing pyrene [35].

The change of I_1/I_3 with the concentration of 12–2–12 Gemini surfactant in pure water and in presence of aqueous lactose and maltodextrin has been plotted in **Fig. 5**. Pyrene senses the polar environment of water molecules before *CMC* and results in higher I_1/I_3 values. However, above the *CMC* where micelles are present; there is solubilization of pyrene molecules in the interior of micellar phase owing to their high hydrophobicity. Micelles act as hydrophobic–like solvent and thus the environment sensed by pyrene is less polar, thereby resulting in the decrease of I_1/I_3 values.

The *CMC* values (Table 2) have been calculated by fitting the plots of I_1/I_3 versus concentration of surfactants to the Sigmoidal Boltzman equation (SBE) [31], as all plots were of sigmoidal nature.

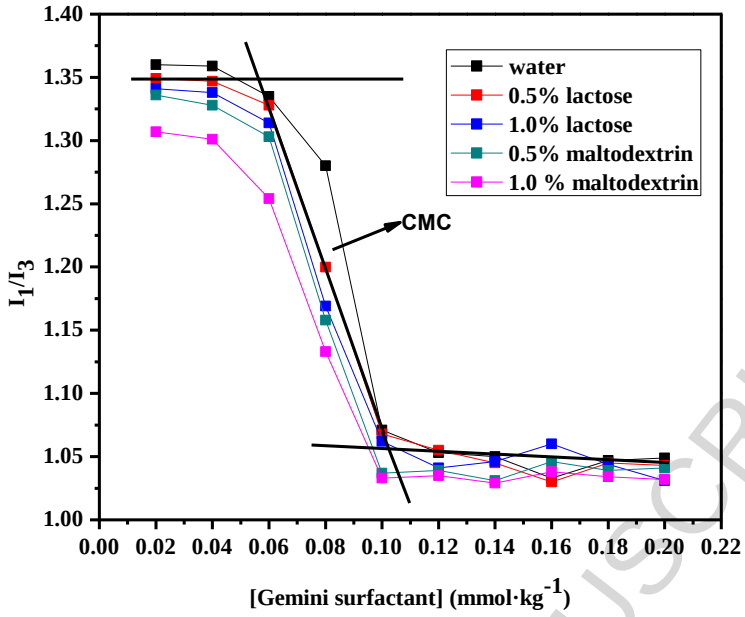


Fig. 5: Plot of I_1/I_3 vs. [Gemini surfactant] in aqueous solution of (0.0, 0.5 and 1.0) % (w/v) lactose/maltodextrin at room temperature (298.15 K).

3.2.3 UV–Visible Measurements

The UV spectral manifestation of pyrene in aqueous surfactant solution is equally important for the estimation of *CMC* of surfactants. Consequently, we have elaborated the potential of pyrene absorption spectrum for the determination of *CMC* of 12–2–12 Gemini surfactant in the absence and presence of carbohydrate in aqueous solutions at room temperature.

Further, pyrene absorption spectrum has evidenced eight strong (s) and weak (w) peaks, at 232w, 242s, 252w, 260w, 272s, 308w, 320s and 336s nm, [36]. It has been shown that the absorbance at 242 nm increases, while above 315 nm, absorbance decreases with the solvent polarity [37]. The micellar interior is non–polar and pyrene, being hydrophobic, is naturally attracted to reside in the non–polar interior as there is no hydrophilic functionality of pyrene. After micellization there is small increase in the UV absorbance which is due to the formation of micelles and incorporation of more pyrene monomers into them [38]. The sum of absorbances of all the four strong peaks (A_T) against the concentration of Gemini surfactant in pure water and in aqueous solution of lactose and maltodextrin has been illustrated in **Fig. 6**. It has been revealed

that in all profiles A_T exhibits sigmoidal increase with the surfactant concentration and therefore, fitting them to the Sigmoidal–Boltzmann equation (SBE).

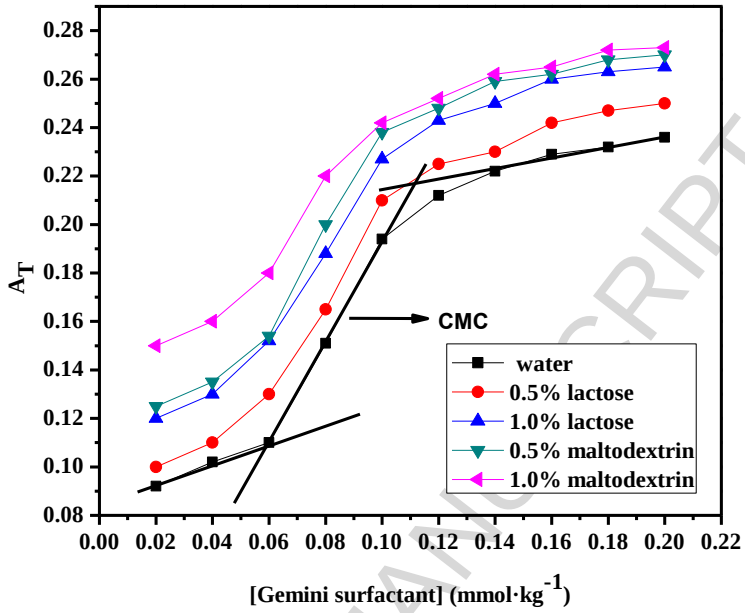


Fig. 6: Plot of A_T vs. [Gemini surfactant] in aqueous solution of (0.0, 0.5 and 1.0) % (w/v) lactose/maltodextrin at room temperature (T=298.15 K).

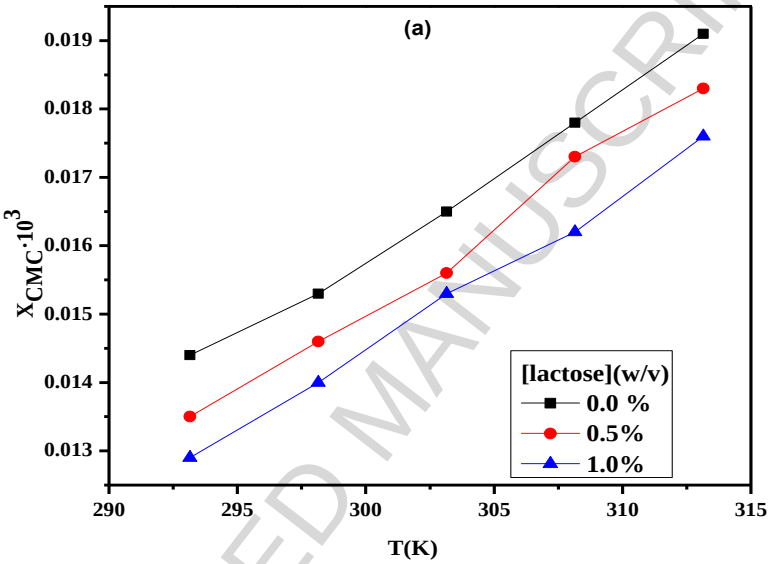
3.3 Temperature dependence of CMC

The effect of temperature on *CMC* or X_{CMC} values of 12–2–12 Gemini surfactant in aqueous solutions of lactose/maltodextrin (0.0, 0.5, and 1.0) % (w/v) have been graphically represented in **Fig. 7**. It has been noticed that *CMC* or X_{CMC} values increase with rise in temperature. The effect of temperature on *CMC* of Gemini surfactant in studied solvent system depends on two opposing factors [39, 26]:

i) The de–solvation of the ionic head groups of Gemini surfactant/carbohydrates by water molecules at lower temperatures (hydrophilic hydration), which favors the micellization and decrease the *CMC* values.

ii) The interruption of the structured water molecules surrounding the non–polar parts of Gemini surfactant/carbohydrates and breaking up of the hydrogen bonds present between different species in the system which oppose micelle formation.

Therefore, the variation of *CMC* depends on the competition of above two factors. In case of 12–2–12 Gemini surfactant, second factor predominates in the temperature range studied which results in the increment of *CMC* values with temperature. Moreover, thermal motion of surfactant and solvent molecules also increases with rise in temperature as a result the formation of ordered micellar structure becomes difficult. This leads to decrease in the aggregation of surfactant monomers and hence increase in *CMC* of the solute.



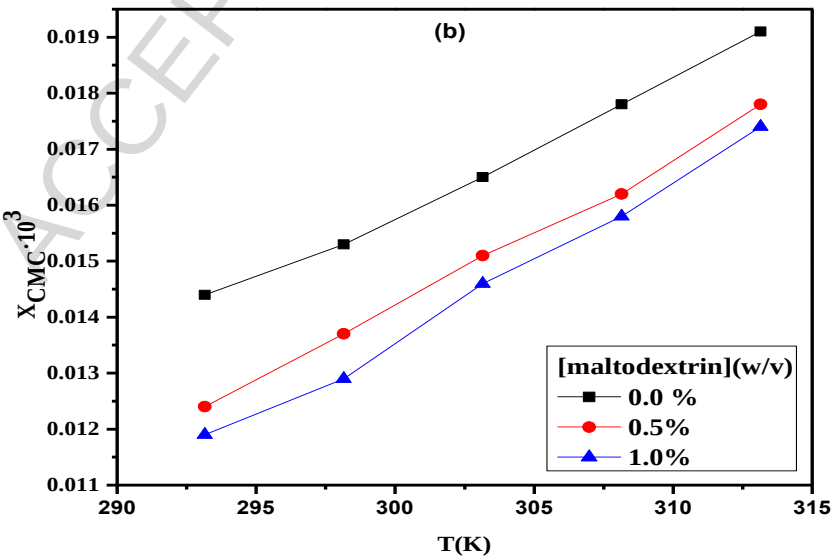


Fig. 7: Plot of X_{CMC} versus temperature for 12–2–12 Gemini surfactant in aqueous solution of (0.0, 0.5 and 1.0) % (w/v) (a) lactose and (b) maltodextrin.

3.4 Thermodynamics of Micellization

Using pseudo phase separation model [40], the standard thermodynamic parameters of micellization for 12–2–12 Gemini surfactant in pure water and aqueous solutions of carbohydrates have been calculated using the X_{CMC} data.

The standard enthalpy of micellization, ΔH_m^o for ionic surfactants is given by the equation [41, 42]:

$$\Delta H_m^o = -2RT^2(1.5-\alpha)[d(\ln X_{CMC})/dT] \quad (1)$$

where $d(\ln X_{CMC}/dT)$ is the slope of the curve plotted between $\ln X_{CMC}$ vs. T and the data so obtained was subjected to least–squares treatment. Here, α is the degree of counter–ion dissociation, which was calculated from equation [42].

$$\alpha = S_2/S_1 \quad (2)$$

where, S_1 and S_2 are the slopes in pre–and post–micellar regions determined from the conductivity graphs with correlation coefficient always greater than 0.990. The standard free energy of micellization, ΔG_m^o and entropy of micellization, ΔS_m^o have been estimated from the following equations [41,42];

$$\Delta G_m^o = 2(1.5-\alpha)RT\ln(X_{CMC}) \quad (3)$$

$$\Delta S_m^o = \Delta H_m^o - \Delta G_m^o/T \quad (4)$$

The values of ΔH_m^o, ΔG_m^o and ΔS_m^o for 12–2–12 Gemini surfactant in aqueous solutions of lactose/maltodextrin have been summarized in **Table 3**.

Table 3: Standard thermodynamic parameters ΔH_m^o, ΔG_m^o and ΔS_m^o of micellization for 12–2–12 Gemini surfactant in aqueous solutions of ([a]m = 0.0, 0.5, 1.0) % (w/v) lactose and maltodextrin at different temperatures (T/K).

	Lactose			Maltodextrin	
Conc. / T (K)	0.0 %	0.5 %	1.0 %	0.5 %	1.0 %
			ΔH_m^o (kJ·mol^{-1})		
293.15	-25.73	-27.74	-27.56	-31.65	-35.62
298.15	-25.99	-28.02	-27.78	-31.83	-35.86
303.15	-26.31	-28.26	-28.12	-32.16	-36.15
308.15	-26.64	-28.56	-28.46	-32.37	-36.45
313.15	-26.89	-28.81	-28.79	-32.57	-36.68
			ΔG_m^o (kJ·mol^{-1})		
293.15	-69.89	-70.73	-70.55	-71.35	-72.53
298.15	-69.05	-69.79	-69.42	-70.41	-71.25
303.15	-68.26	-68.77	-68.59	-69.27	-69.89
308.15	-67.52	-67.77	-67.94	-68.17	-68.82
313.15	-66.66	-66.90	-67.09	-66.91	-67.55
			ΔS_m^o (kJ·mol^{-1}·K^{-1})		
293.15	0.151	0.147	0.147	0.137	0.126
298.15	0.144	0.140	0.140	0.129	0.119
303.15	0.138	0.134	0.133	0.122	0.111
308.15	0.133	0.127	0.128	0.116	0.105
313.15	0.127	0.122	0.122	0.110	0.099

[a]m is the percentage of lactose and maltodextrin(w/v) in water. Standard uncertainties, u, are u(T) = 0.01 K and u(CMC) = $0.01 \cdot 10^{-3}$ mol·kg^{-1}, (level of confidence = 0.68).

It can be visualized from Table 3 that the ΔG_m^o values for 12–2–12 Gemini surfactant are negative in pure water and in aqueous solutions of lactose/maltodextrin indicating micellization to be a spontaneous process and micelles are thermodynamically stable in all studied systems. It

has been observed that ΔG_m^o values increase i.e. become less negative with temperature. This may be attributed to the fact that as temperature increases, enhancement of molecular motions and promotion of repulsions between head groups takes place resulting in disaggregation of surfactant monomers which inhibits micellization process [42]. The ΔG_m^o values are more negative in case of maltodextrin as compared to lactose indicating higher steadiness of the system which may be due to stronger driving forces for micellization. This enhanced stability in case of maltodextrin may be due to the structural modification in the system as we move from lactose to maltodextrin i.e. presence of additional hydrophobic region.

Negative values of ΔH_m^o in present case depicts that process of micellization is exothermic in nature which may be the consequence of possible interactions between surfactant–solvent and solvent–solvent molecules resulting into release of water molecules surrounded by a hydrophobic tail during their transformation from bulk phase to micelle. Moreover, the negative values of enthalpy indicate that the London dispersion forces also play an important role in the micellization process for Gemini surfactant–carbohydrate system. It can be seen from the **Table 3** that ΔH_m^o values becomes more negative with temperature because of increased contribution of ΔH_m^o towards free energy as a result of reduction of hydrogen bonds between solvent molecules and therefore lesser energy required to break up the water cluster [42]. However, the values further decrease with the rising concentration of carbohydrates which may be due to the decreased energy requirements to break up the ice–berg structure surrounding the hydrophobic part of the mixture [43, 44].

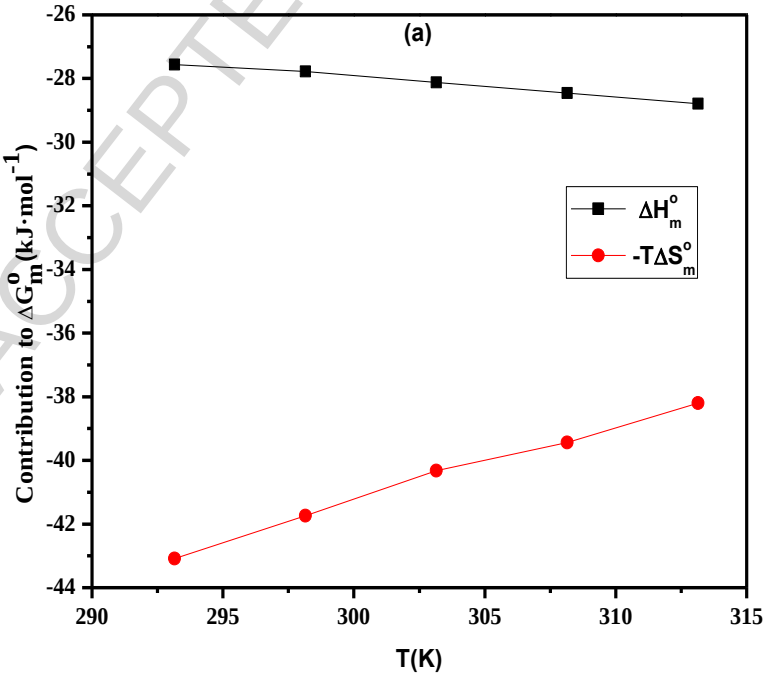
The values for ΔS_m^o have been found to be positive for 12–2–12 Gemini surfactant in the absence and presence of both additives i.e. aqueous solution of lactose/maltodextrin. This may be attributable to the melting of "ice–bergs" or flickering structures around hydrocarbon tails of surfactant monomers and increased randomness of the hydrocarbon chains in the micellar core [16]. Also ΔS_m^o values decrease with rise in temperature. This can be explained by taking two opposing processes into account [45, 46]:

i) disruption of three–dimensional water matrix around the hydrocarbon tails of surfactant monomers due to their incorporation into micelles resulting into increase in randomness and hence entropy.

ii) arrangement of disordered monomers into more ordered surfactant aggregates leading to negative change in entropy.

In studied system, second factor predominates and hence resulted in smaller value of ΔS_m^o with temperature. It has been further found that values of ΔS_m^o are greater for aqueous 12–2–12 Gemini surfactant as compared to those in the presence of carbohydrates as ordering of randomly oriented cationic surfactant from the solvated form to micellar structure dominates over destruction of water structure [44, 47]. Comparatively, maltodextrin lowers ΔS_m^o values of 12–2–12 Gemini surfactant to a larger magnitude than lactose due to enhanced micellization in former case. However, ΔS_m^o values of Gemini surfactant in aqueous lactose are almost independent of concentration, whereas the same shows an observable decrease in case of maltodextrin.

A curious investigation of Table 3 shows that ΔG_m^o values are practically independent of temperature and nature of carbohydrate as well. This behavior reasonably accounts for the compensation between ΔS_m^o and ΔH_m^o values leaving ΔG_m^o almost unaffected. However, as ΔG_m^o is the sum of the enthalpic and entropic contributions, with increase in temperature, the enthalpic contribution to the free energy increases, whereas the entropic contribution decreases as can be seen from **Fig. 8.**



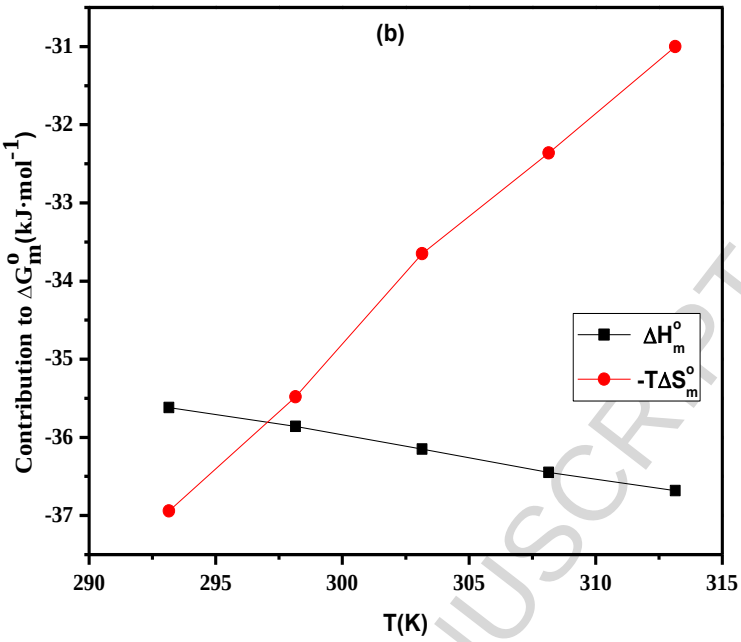


Fig. 8: Representative Plots of contribution of ΔH^o_m and $-T\Delta S^o_m$ to ΔG^o_m versus temperature for 12–2–12 Gemini surfactant in 1.0 % (w/v) (a) lactose and (b) maltodextrin.

5. Conclusion

The addition of carbohydrates to aqueous 12–2–12 Gemini surfactant has been found to facilitate micellar behaviour of surfactant as revealed by the determined CMC order i.e. no additive > lactose > maltodextrin. This may be attributed to the fact that, the structural modification has been imparted to the system by these bio-molecules because of presence of more hydrophobic region. In addition, the temperature has also been found to be decisive factor in the micellization of the surfactants. With rise in temperature, the *CMC* increases which may be due to the interruption of structured water molecules surrounding the non–polar parts of Gemini surfactant/carbohydrates system. The process of micellization is of spontaneous nature as shown by thermodynamic parameters and both hydrophobic interactions and London dispersion forces seem to play an important role for the same. The results obtained from the conductivity measurements are strongly supported by those obtained from fluorescence and UV-Visible probe studies. The findings of the study may form the basis for utilizing surfactants in presence of carbohydrates especially for industrial applications with the eventual aim of producing eco–friendly and sustainable surface active formulations.

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Highlights

- Analysis of Micellar modulation of 12–2–12 Gemini surfactant in presence of carbohydrates by conductometry and spectroscopic studies.
- A decrease in the CMC values of 12–2–12 Gemini surfactant has been observed in the presence of lactose/maltodextrin.
- Enhancement of hydrophobic region in case of maltodextrin results in more decrease of CMC values as compare to lactose.
- Temperature dependence of *CMC* has been employed to compute standard thermodynamic parameters of micellization.
- The entropy dominance switched to enthalpy dominance around the midpoint of the temperature range examined.