Analysis of Micellar behavior of as Synthesized Sodium itaconate Monoesters with various Hydrophobic chain lengths, in Aqueous media

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Abstract

Polymerizable surfactants belong to the class of n-alkyl itaconate monoesters are synthesized using itaconic anhydride and the n-alkanols, with n from C10 to C16 chain lengths as precursors. The seven homologues of itaconate monoesters(IAn) synthesized are treated with Sodium Hydroxide (NaOH) solution to result in sodium n-alkyl itaconate mono esters which act as anionic surfactants in aqueous medium. The structural characterizations of IAn are carried out using FTIR and ^1HNMR measurements. Specific conductance and UV absorbance values are determinedat different concentrations of surfactant and NaOH in aqueous medium. The critical micelle concentration (CMC), the fractional charge per micelle (α) and the standard free energy change of micellisation (ΔG^0_{mic}) values are determined for each of the IAn surfactants at 25^0C. The effect of hydrophobic chain length (Cn) on the micellisation parameters CMC, α, and ΔG^0_{mic} are depicted using the three dimensional (3D) plots with Cn and NaOH concentration dependences. The CMC values decreased gradually with increase in Cn due to raise in the hydrophobicity of the micelle core, while α values increased up to C14 homologous and further decreased with increase in Cn due to chain folding inside the micelle core. The synthesized polymerizable surfmers could find application in the production of stable functional polymeric nano particles.

Keywords: Polymerizable surfactants, Itaconate mono ester, micellisation, critical micelle concentration (CMC), chain length effect, Hydrophobicity.

Introduction

Itaconic acid (ItA) represent the vinyl organic with dicarboxylic acid functionality. The mono esters, derived from Itaconic acid, can form a library of derivatives with different hydrocarbon chain lengths when reacted with various chain length alkanols. It A mono esters exhibit two potential properties such as the surface activity due to the amphiphilicity and polymerizable nature due to the vinyl group. ItA is eco-friendly and it can be produced from ascorbic acid or through fermentation of molasses by Aspergillusterreus[1-3]. The n-alkyl itaconate mono esters (IAn) are used to functionalise homo and copolymer composites prepared through emulsion polymerizations. Reports exist on the single step approach preparation of long chain alkyl mono esters of itaconic acid using itaconic anhydride and the corresponding long chain alcohol [4,5]. In aqueous NaOH solutions, Sodium alkyl itaconate mono esters (IAn) are formed which generate anionic micelles similar to anionic alkyl surfactants[6]. The CMC and the fractional charge per micelle (α) values are determinedfrom the specific conductance and UV-absorbance dependences with surfactant concentration [7,8]. The same are carried out in different concentration of NaOH medium. Here sodium itaconate mono esters (IAn) with alkyl chain lengths varying from decyl (C10) to hexa-decyl (C16) are synthesised and arecharacterised using ^{1}H NMR, FTIR, and UV spectra.

The 3D surface plots are created with the CMC and α value at different NaOH concentrations and Cn values. From the plots, it is observed that the CMC values decrease from C10 to C16 IAn homologues and while α values initiallyincrease with the increase in chain lengthfrom C10 to C14 and then decrease with C14 to C16. The results of the investigations are presented and possible discussions are put forth[9-12].

Material and Methods

Material: Itaconic anhydride alcohols with chain length from C10 – C16 are purchased from Alfa Aesarwith 99.9% purity. Triple distilled water, was used in all preparation of aqueous solutions. Sodium hydroxide pellets were purchased from Loba Chem India Limited. ^{1}H NMR spectra were performed on Bruker 400 MHz spectrometer using $CDCl_3$ as solvent. FT-IR spectra were recorded for the corresponding samples as KBr pellets using BRUKER (TENSOR 27) in the region 4000-400 cm^{-1}. UV-Visible spectra were carried out using Techcomp 8500 spectrophotometer.

Synthesis of itaconate mono ester: 2.0g of itaconic anhydride (18mM) and 3.14 g of decanol (20mM) were dissolved in10mL of dry chloroform with constant stirring at 80^0C (oil bath) for 8 h. The excess solvent was removed using rotary evaporator. The obtained product was further dissolved in n-hexane and allowed to cool at-2^0C to yield white crystals of decyl itaconate ester.

The above reaction was repeated multiple times for reproducibility. Also in the place of decanol each one of the following monohydric alcohols at 20mM concentration were used undecanol (3.44g), dodecanol (3.65g), tridecanol (3.94g), tetradecanol (4.22g), pentadecanol (4.5g) and hexadecanol (4.75g). A simplified workup procedure, reported earlier, was followed inthe preparation of various hydrophobic chain length itaconate mono ester surfactants as shown in scheme 1[4]. It was found that the use of itaconic anhydride with a marginal excess of the long chain alcohols resulted in excellent yield (92%) with high purity. The as synthesised seven surfactants belonging to the itaconate mono esters family with varying chain lengths from C10 to C16 are collected, purified by recrystallization and characterised.
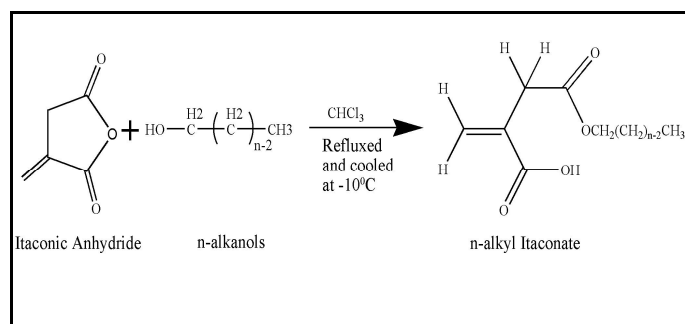
Scheme-1
Synthesis of alkyl β-mono ester itaconate

Results and Discussion

Structural characterization of alkyl β mono ester itaconates: The UV, FTIR and ^{1}HNMR spectroscopic measurements are made using the freshly recrystallized samples. In figure1A the UV absorption spectra stacked with various dilution of decyl mono ester of itaconic acid, has been presented. A prominent and smooth peak around 210nm was found with absorbance values sensitive to the compositions of the surfactant. Also, with further decrease in concentration, the peak is blue shifted to within 5nm[13]. All the different chain length itaconate esters produced the similar UV spectra because the UV active functional group remains the same. The presence of the peak may be attributed to the π- π* transition of the double bonds present in – C=C- and >C=O groups. This observation is found useful for the CMC determination.

In figure 1B, the FTIR spectra of (a) decyl- and (b) pentadecyl-itaconate esters are shown. The 1723cm^{-1}peak is attributed to carbonyl stretching. Moreover, the bands at 2950cm^{-1}–2820cm^{-1}are due to asymmetrical and symmetrical C–H stretching vibrations of methylene and methyl groups respectively. The -CH$_2$- bending and C-CH$_3$ bending was appearedat 1458cm^{-1} and 1380cm^{-1} respectively. The finger print region 1000cm^{-1}-1400cm^{-1} of the FTIR spectra detects the chain length variations due to the addition of -CH$_2$- groups into each of the homologue molecule. The peaks at 1686cm^{-1} and 1635cm^{-1} are attributed to thevinyl group vibrations. The weak vibrational bands near

722cm^{-1} are due to thebending vibrations of (CH$_2$-)$_n$ (where n $\geq$ 4). The strong peaks at 1635cm^{-1}-1723cm^{-1} are attributed to C-O stretching vibrations of ester group. The bending vibration of methylene of the vinyl group appears at 920cm^{-1}-988cm^{-1}. The absence of peaks in the region 1870cm^{-1}-1740cm^{-1} and around 3400 cm^{-1}-3300cm^{-1} indicate the absence of un-reacted anhydride and alcohols. These data indicate that the starting materials are completely absent in the itaconate mono ester products. The attachment of the long alkyl chain from the alcohol reactant to the ester product is revealed by the prominently increasing intensity peak at 2850cm^{-1} while its counterpart peak at 2958cm^{-1}with decreasing intensity. As the chain length increases the transmittance intensities near 450cm^{-1}-650cm^{-1} are decreased and the peaks are shifted to shorter wave number which may be attributed to chain folding effect.
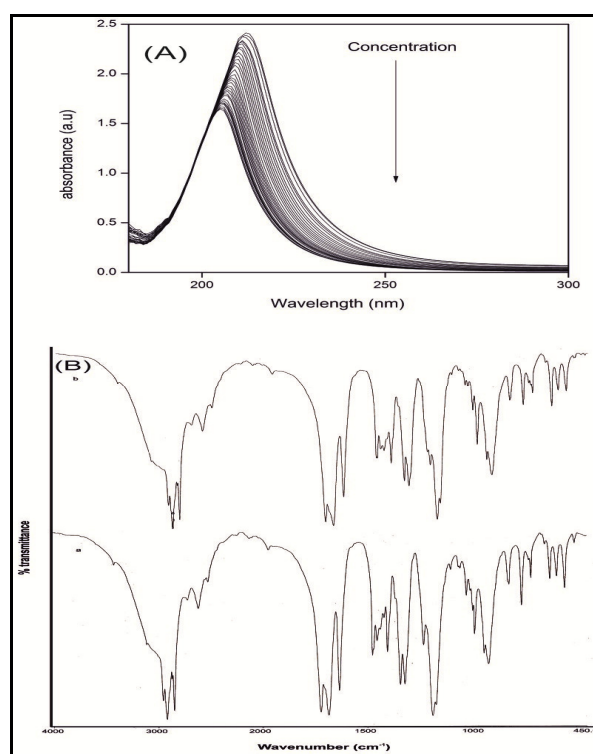

Figure-1
(A) Decyl itaconate [1x10^{-3}M] at various decreasing concentrations, in 0.1M aqueous NaOH solutions, (B) FTIR spectra of different chain lengths (Cn) Itaconate β ester surfactants in KBR pellet at 298K (a) decyl- (b) pentadecyl,-itaconate β-monoesters

The figure 2 shows the ^{1}H NMR of (A) Decyl- and (B) Penta decyl-itaconate mono esters. The polymerizable surfmers show peaks around 1.0 to 1.5 ppm which are due to (-CH$_2$-)$_n$ groups. The height of the peak in this region significantly increases with the Cn value of surfmers from C10 to C16 homologues and this increase corresponds to increase in (-CH$_2$-) units. The ^{1}H NMR spectra exhibited following signals at δ(ppm) for all the chain length variation of Itaconate mono esters:δ_H 6.31(s,1H), 5.69(s,1H,), 4.07(t,2H), 3.32(s,2H), 1.63(m,2H), 1.26(br s,2(n-

3)H), 0.87(t,3H). The ^{1}H NMR and FTIR spectra reveal that the synthesised β-mono esters of Itaconic acid show the presence of both vinyl, and n-alkyl ester functional groups in the IAn molecules with varying chain lengths.
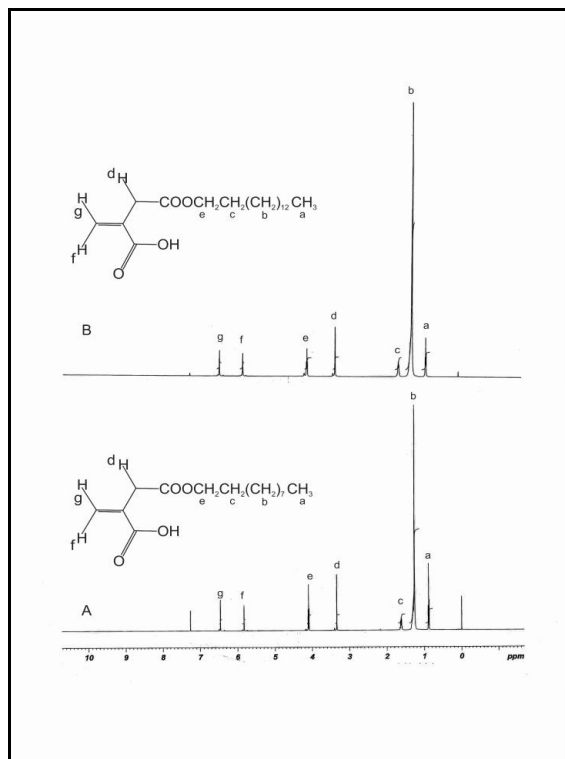

Figure-2
^{1}**H NMR spectra of (A) decyl- (B) pentadecyl-itaconate β ester surfmers in CDCl$_3$**

Micellisation studies: Optical density measurements: The itaconate mono ester compounds, synthesised in this work, dissolved in aqueous sodium hydroxide solution and the UV spectrum given in figure 1A showed a characteristic λ_{max} peak at 205nm. As the concentration of the surfactant (Cs) was increased from 0.1mM to 10mM the peak undergoes a red shift to 212nm. This effect was seen in all the chain lengths of surfactants from C10 to C16. The optical density (O.D) values corresponding to 205nm was plotted against the Cs. Such plots are generated for each chain length variation in IAn surfactant.

In figure 3 the break point in the plot corresponds to the CMC value of the respective chain length of the surfactant.

Inset figure in figure 3, containsthe UV spectra of decyl itaconate (at various decreasing concentrations). The UV spectra for other surfactant chain lengths are found to be similar. Since there is no predominant change in the spectral characteristics with increase in chain length, itmay be considered that the UV active functional group remains the same for all the Cn surfactants of IAn monoesters.

In table 1, the CMC values found from O.D measurements are given. It is found that when the chain length is increased from C10 to C16 the CMC values are decreased. This is in agreeable situation since greater the hydrophobic chain length, the micellisation factors are more favourable and CMC values are reduced significantly[14,15].
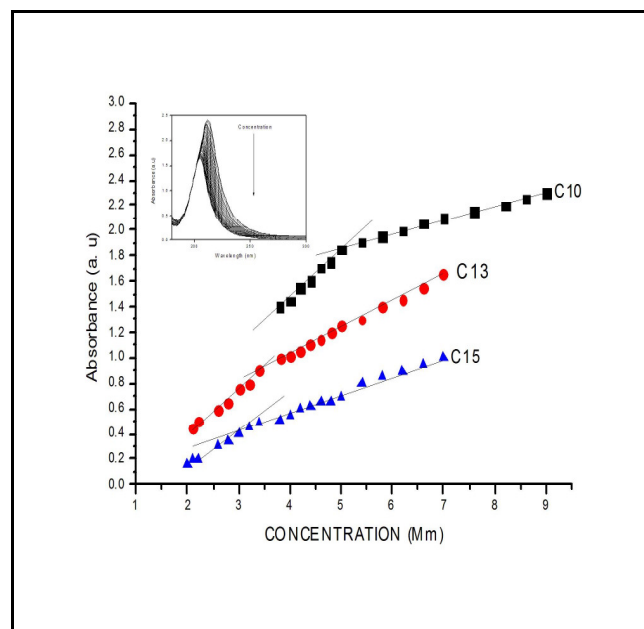

Figure-3
Optical density-concentration plots of decyl, tridecyl and pentadecyl of Itaconate β ester and insert in figure contains UV spectra of decyl itaconate at various decreasing concentrations

Table-1
CMC and α value of Itaconate β ester surfactants with varying alkyl chain length (Cn) in the presence of 1M NaOH from (a) conductivity and (b) OD measurements

Cn of surfactants	Critical micelle concentration (mM)		α
	a (in 1.0 x10^{-4})	b (in 1.0 x10^{-4})	
C10	5.01	5.01	0.55
C11	4.75	4.71	0.58
C12	4.07	4.06	0.62
C13	3.63	3.60	0.79
C14	3.24	3.12	0.88
C15	2.99	3.00	0.85
C16	2.20	2.30	0.80

Specific conductivity studies: In order to estimate the micelle parameters such as fraction of charge per micelle (α), CMC values and free energy change of micellation values, the specific conductivity measurements on the various Cs solutions are made. The conductance profiles of C10 to C16 chain length surfactants in the presence of NaOH aqueous solution are presented in figure 4 A and figure 4B. The critical micelle concentration (CMC) was calculated from the intersection points below and above the CMC values.

It is found that the specific conductance (κ) values generally decrease with increase in the chain length of surfmers. This effect is attributed to the bulkiness of the anionic part of the homologues. The CMC values decreased gradually with increase in the chain length of the surfactants[16-18]. In table 1, the CMC values and the fractional charge of the micelle (α) are presented. It is found that the CMC values coincide with those determined from the O.D measurements within the error limits. The ratio of the slopes of the post micellar to the pre-micellar linear plots, gives the value of 'α'. It is found from the table 1, the αvalues increase from C10 to C14 carbon chain length while from C14 to C16 chain lengths of the surfactant show a decrease. For the C10 to C14 chain length homologues, the radius of the micelle formed increases, since the length of the hydrocarbon constituting approximately the radius of the micelle increases. The micellisation effect screens the head group charge repulsions so that the counter-

ion binding decreases[19-21]. This effect results in an increase in the α value of the micelle. This aspect cannot be extended to C14 and C16 chain length surfactants, because α values show a decreasing trend. When the chain length of the hydrocarbon part increases further, chain folding may result based on thermodynamic considerations which cause an increase in the counter-ion bindings.This effect results in the overall decrease in α value. Tetra decyl itaconate ester (C14 system) is present in the transition in the trends of αvalue from C10-C16 chain lengths.According to the pseudo phase separation model, the standard free energy change of micellation for the ionised surfactantscan be known from the expression, as follows:

$$\Delta G^0_{mic} = (2 - \alpha) RT\, 2.303 \log X_{cmc}$$

Where, X_{cmc} is the mole fraction of the surfactant at the CMC value. Likewise, the calculated ΔG^0_{mic} values are presented in table 2. In the presence of NaOH solution, negative values of ΔG^0_{mic} are found indicating the spontaneous and favourable forces to operate for micellation process.The chain length effect shows thatC10 to C14 systems, produce more negative values than the C14 to C16. Since ΔG^0micellisation values critically depend on the CMC and fractional charge per micelle values, the combined effects of electrostatic and hydrophobic force ascertains the stability of micelles formed in the NaOH medium
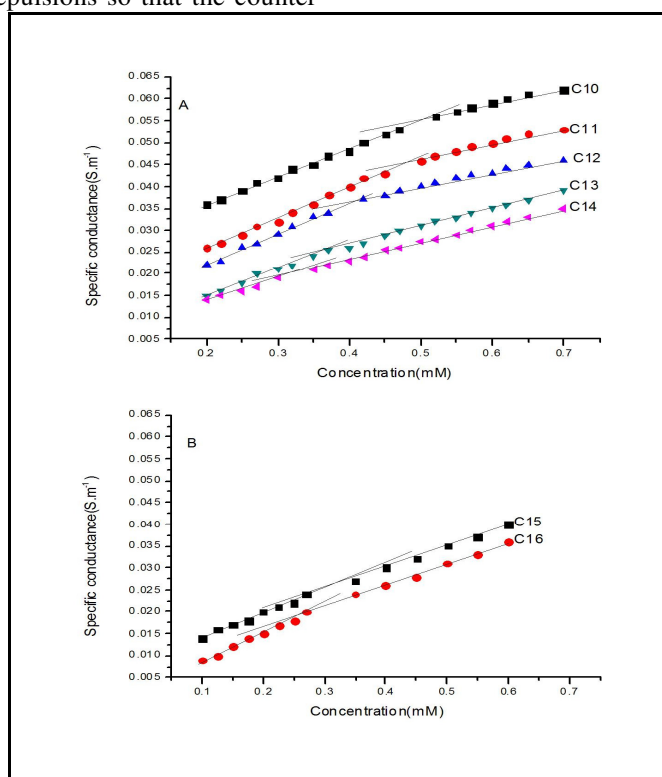

Figure-4

A Specific conductivity-concentration plots of monodecyl, unidecyl, do decyl, tridecyl, tetra decyl and hexadecyl itaconate β ester surfactants in 1M NaOH solution. (1mho.m⁻¹= 1 siemens.m⁻¹),B specific conductivity-concentration plots of pentadecyl and hexadecyl itaconate β ester surfactants in 1M NaOH solution. (1mho.m⁻¹= 1 siemens.m⁻¹)

Table-2
ΔG^0_{mic} kJ mol^{-1} values of various chain length of alkyl itaconate β ester surfmers at T= 298K,
with NaOH concentration variation

Cn	ΔG^0_{mic} kJ mol^{-1}			
	0.05MNaOH	**0.1 M NaOH**	**0.5 M NaOH**	**1M NaOH**
C10	-38.54	-38.88	-40.34	-41.80
C11	-38.29	-38.84	-39.99	-41.12
C12	-38.06	-38.74	-39.66	-40.49
C13	-33.70	-34.33	-34.93	-35.85
C14	-33.13	-33.42	-33.72	-33.50
C15	-34.19	-34.48	-34.73	-34.63
C16	-35.08	-35.18	-35.44	-36.44

Effects of concentration of sodium hydroxide medium: In the absence of alkaline medium, alkyl itaconate mono ester behaves as a non-ionic surfactant and exhibit limited solubility. For the facile surface activity and the micellation of surfmers, sodium hydroxide aqueous medium is preferred. In NaOH solution, the itaconate mono ester dissolves resulting in the sodium salt of carboxylate anion surfmers. As the concentration of NaOH increases in the medium, the solubility of the surfmer also increases. Keeping the constant alkyl chain length, it is found that the CMC values get increases with increase in concentration of NaOH, in which NaOH acts assolubilising and proton ionizing medium for the IAn monoester. This causes the CMC increase effect with increase in NaOH concentration. The effect of NaOH concentration on α value can be rationalized similarly. The fraction of charge per micelle (α) value decreases with increase in NaOH concentration because the counter ion binding per micelle increases. The negative values of standard free energy change of micellisation clearly indicate that NaOH medium favours micellisation and the combined effects of n-alkyl chain length of the surfactant and its composition determine the micellar parameters.

3D plots of [NaOH]−C$_n$−CMC/α: In figure 5 A and figure 5B, 3D plot of micelle parameters of alkyl itaconate β-esters with varying chain lengths are presented. To study the effect of hydrocarbon chain length on the micellisation parameters CMC and α, 3D plots are chosen as they expose the results in a better way. NaOH medium influences strongly the onset of CMC values and the corresponding resultant charge of the micelle, keeping the alkyl chain length constant. In table 3, the role of NaOH on the micellisation behaviour of various alkyl chain length surfmers is presented as profiles.

There is continuity in CMC increase with the corresponding increase in the NaOH concentration. However, when the hydrocarbon chain length is increased from C10 to C16, the values of micellisation, CMC show a regular decrease while α value seem to change the trend of increasing and decreasing effects at C14 surfmer. In the 3D plot of figure 5 (A), this becomes clearly visible.

In figure 5B, the 3D profile of sodium hydroxide concentration, n-alkyl chain length (C$_n$), and α values are presented. During micellisation, the inter-head group charge repulsion decreases when the radius of the micelle increases. The alkyl chain length increase in the surfmer increases the micelle radius and the inter-head group distance increases. This effect causes an increase in the charge per micelle (α). An increase in α value measured brings out the hydrophobic-hydrophobic interactions that prevail in the hydrophobic core of the normal micelle. From C10 to C14, the increase in the alkyl chain length which leads to increase in the radius of micelle. As a micelle grows bigger, head group repulsion reduces and charge per micelle increases. After C14, chain length of surfmer increases to C15 and C16 bringing a decrease in α values. That is, the radius of the micelle slightly decreases so that the counter-ion binding increases. Increase in the counter-ion binding decrease α values. Such a change in α value occurs near the C14 surfactant chain length which is clearly depicted in the 3D profile in the figure5B. The chain folding effect increases with increase in C$_n$, when n≥14 the counter ion binding increases and fractional charge per micelle decreases. As the sodium hydroxide concentration increases unconditionally CMC increases. It may be seen that α values decrease. In the case of increase in NaOH concentration, the counter-ion binding also increases[22,23].
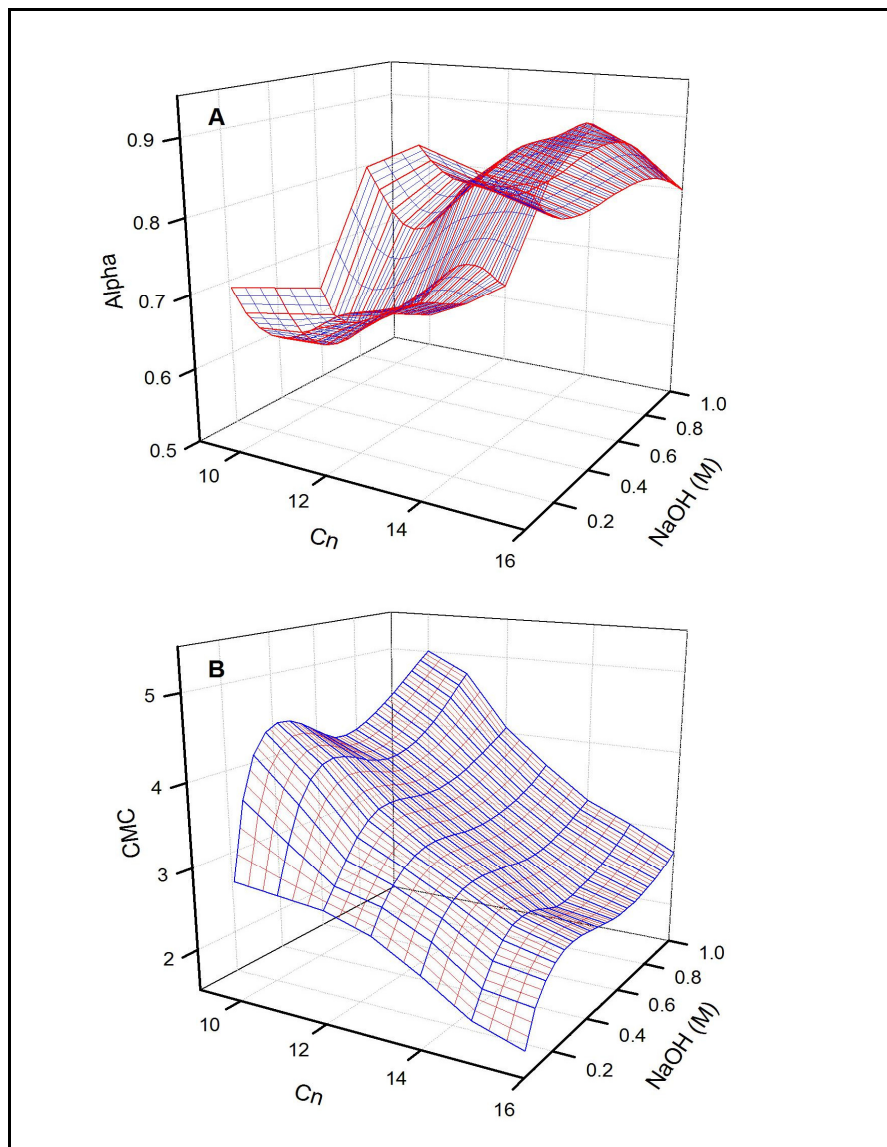
Figure-5
(A) 3D plot of Cn-[NaOH]-CMC dependences of alkyl itaconate β ester surfmers, (B) 3D plot of Cn-α-[NaOH] of alkyl itaconate β ester surfmers

Table-3
Effect of NaOH concentration on the CMC and α value of Itaconate β ester surfactant with varying Cn, from conductivity measurement values

Cn of surfactants	0.05 M NaOH		0.1M NaOH		0.5M NaOH	
	CMC (M) (in 1 x 10^{-4})	α	CMC (M) (in 1 x 10^{-4})	α	CMC(M) (in 1 x 10^{-4})	α
C10	2.94	0.72	3.83	0 .68	4.21	0.67
C11	2.88	0.73	3.43	0.69	3.92	0.64
C12	2.82	0.74	3.03	0.70	3.64	0.66
C13	2.65	0.89	2.93	0.86	3.28	0.83
C14	2.34	0.92	2.63	0.9	2.96	0.88
C15	1.98	0.90	2.24	0.88	2.56	0.86
C16	1.80	0.88	2.17	0.86	2.48	0.84

Conclusion

The CMC values decreased gradually with increase in Cn due to raise in the hydrophobicity of the micelle core, while α values increased up to C14 homologous and further decreased with increase in Cn due to chain folding inside the micelle core. The synthesized polymerizable surfmers could find application in the production of stable functional polymeric nano particles.

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