Synthesis and physicochemical properties of non-ionic and cationic surfactants derived from methionine

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Surfactants

Key ingredients in detergents and cosmetics

Good antibacterial activity

Good foaming ability

Cleaning property

Benefits

Drawbacks

Antimicrobial resistance

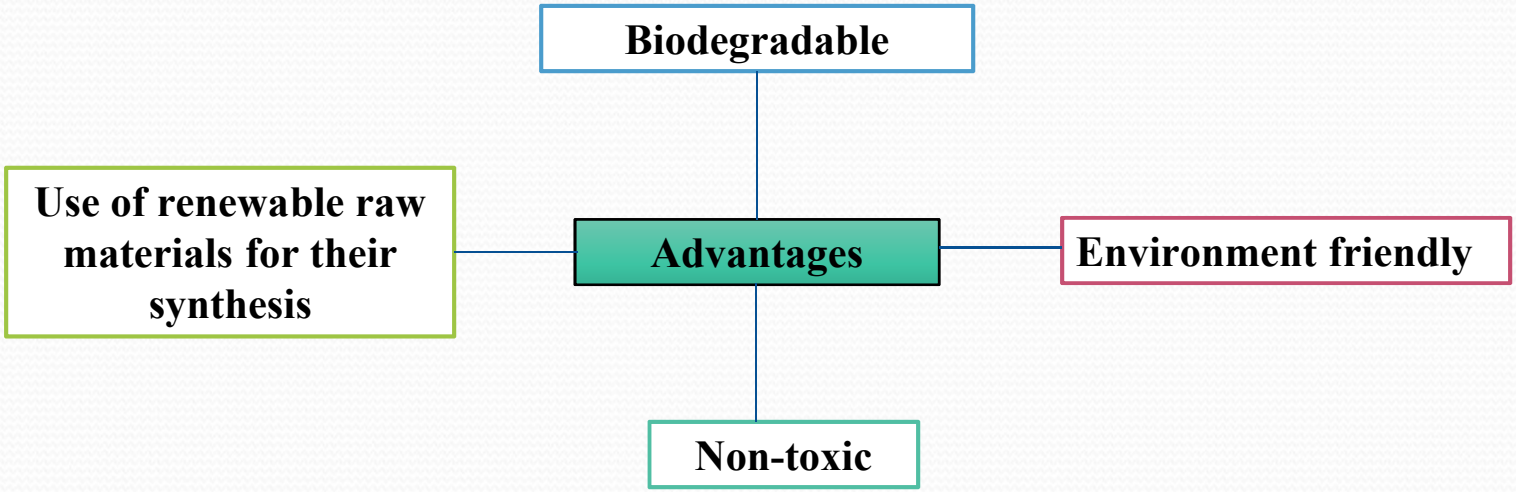
Toxic

Non-biodegradable

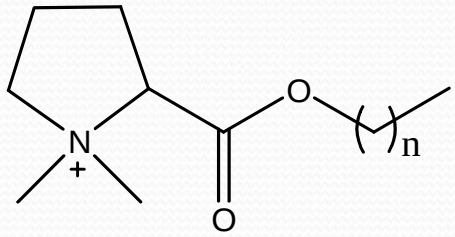
Petroleum based chemicals

Amino acid based surfactants

- Consists of an amino acid head group linked to a long fatty acid/alcohol chain
- Can be used as alternative to conventional surfactants



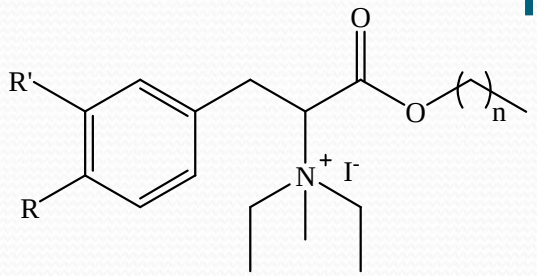
Examples of amino acid surfactants reported



Proline-based surfactants

n= 15

n= 7, 9, 11, 13, 15

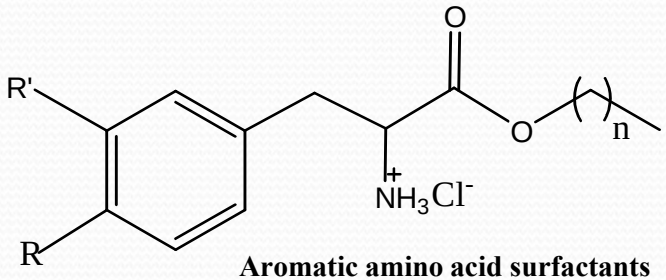


Aromatic amino acid-based quaternary ammonium surfactants

R= R'= H; n= 9, 11, 13, 15

R=OH, R'= H; n= 9, 11, 13, 15

R= R'= OH; n= 9, 11, 13, 15



Aromatic amino acid surfactants

R=R'= H, n=7-19

R=OH, R'=H, n=7-21

R= R'=OH,' n=7-13

Joondan, N., Jhaumeer-Laulloo, S., Caumul, P., 2014. Microbiol. Res. 169, 675-685

Joondan, N., Caumul, P., Akerman, M., Jhaumeer-Laulloo, S., 2015 Bioorg. Chem. 58, 117-129

Joondan, N., Jhaumeer-Laulloo, S., Caumul, P., 2015. J. Surfactants Deterg. 18, 1095-1104

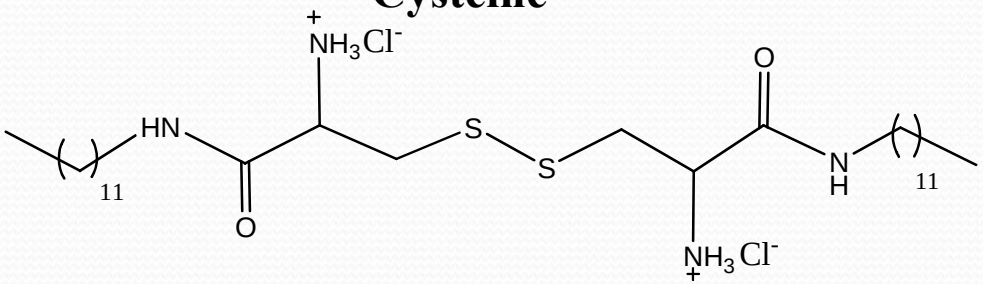
Joondan, N., Jhaumeer-Laulloo, S., Caumul, P., Marie, D.E.P., Roy, P., Hosten, E., 2016. Colloids. Surf. A. Physicochem. Eng. Asp. 511, 120-134

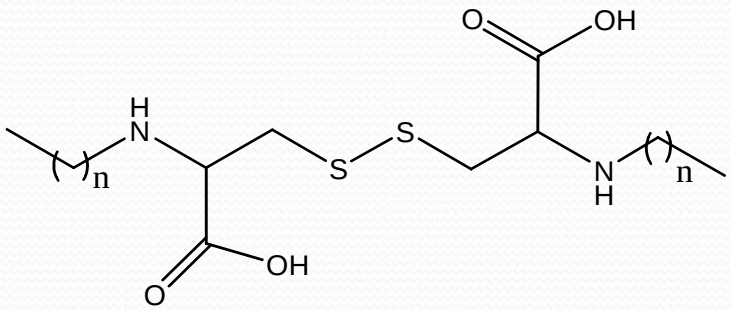
Joondan, N., Caumul, P., Jhaumeer-Laulloo, S., 2017. J. Surfactants Deterg. 20, 103-115

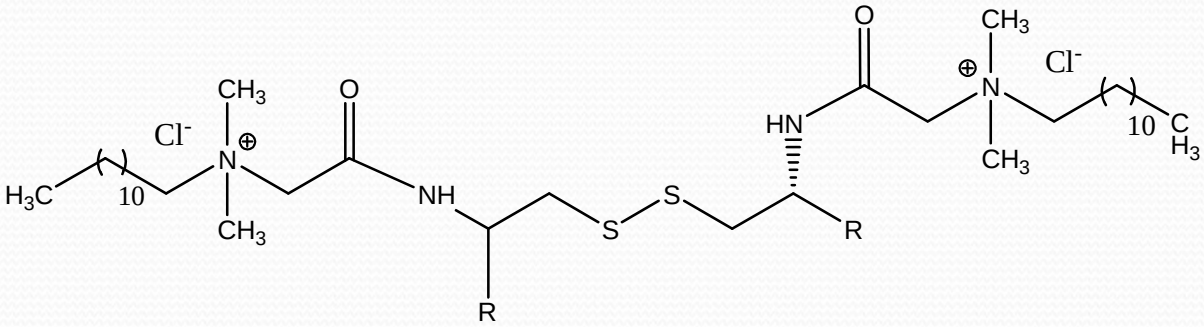
Baczko, K., Larpenta C., Lesot, P., 2004. Tetrahedron: Asymmetry, 15, 971–982

Sulfur-based Amino acid surfactants

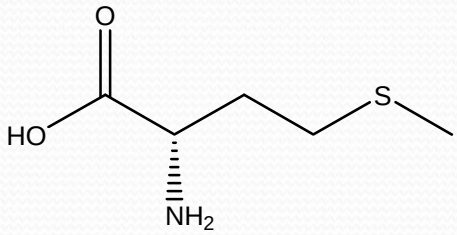
Cysteine







Methionine



However, there is very little report on surfactants derived from methionine

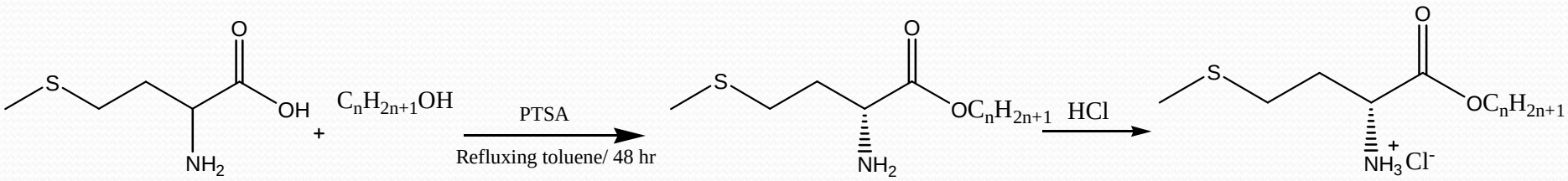
Branco, M.A., Pinheiro, L., Faustino, L., 2015. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 480, 105-112

Fan, H., Han, F., Liu, Z., Qin, L., Li, Z., Liang, D., Ke, F., Huang, J., Fu, H., 2008. Journal of Colloid and Interface Science, 321, 227-234

Pinazo, A., Diz, M., Solans, C., Pes, M.A., Erra, P., Infante, M.R., 1993. Journal of American Oil Chemists' Society, 70, 37

Yoshimura, T., Sakato, A., Tsuchiya, K., Ohkubo, T., Sakai, H., Abe, M., Esumi, K., 2007. Journal of Colloid and Interface Science, 308, 466-473

Synthesis of methionine *O*-alkyl esters and their hydrochloride derivatives

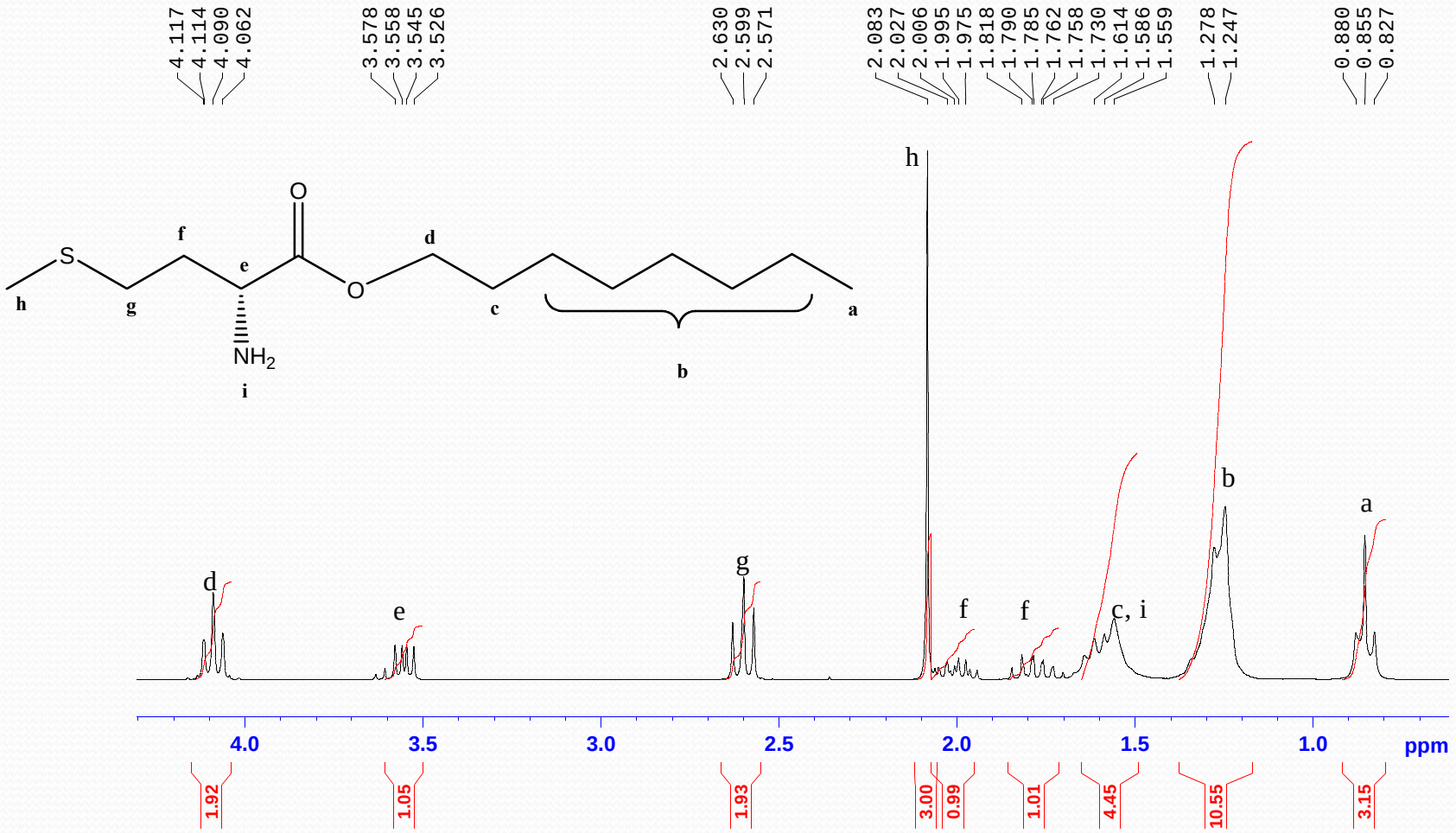


1a: n= 8; 1b: n=10; 1c: n=12

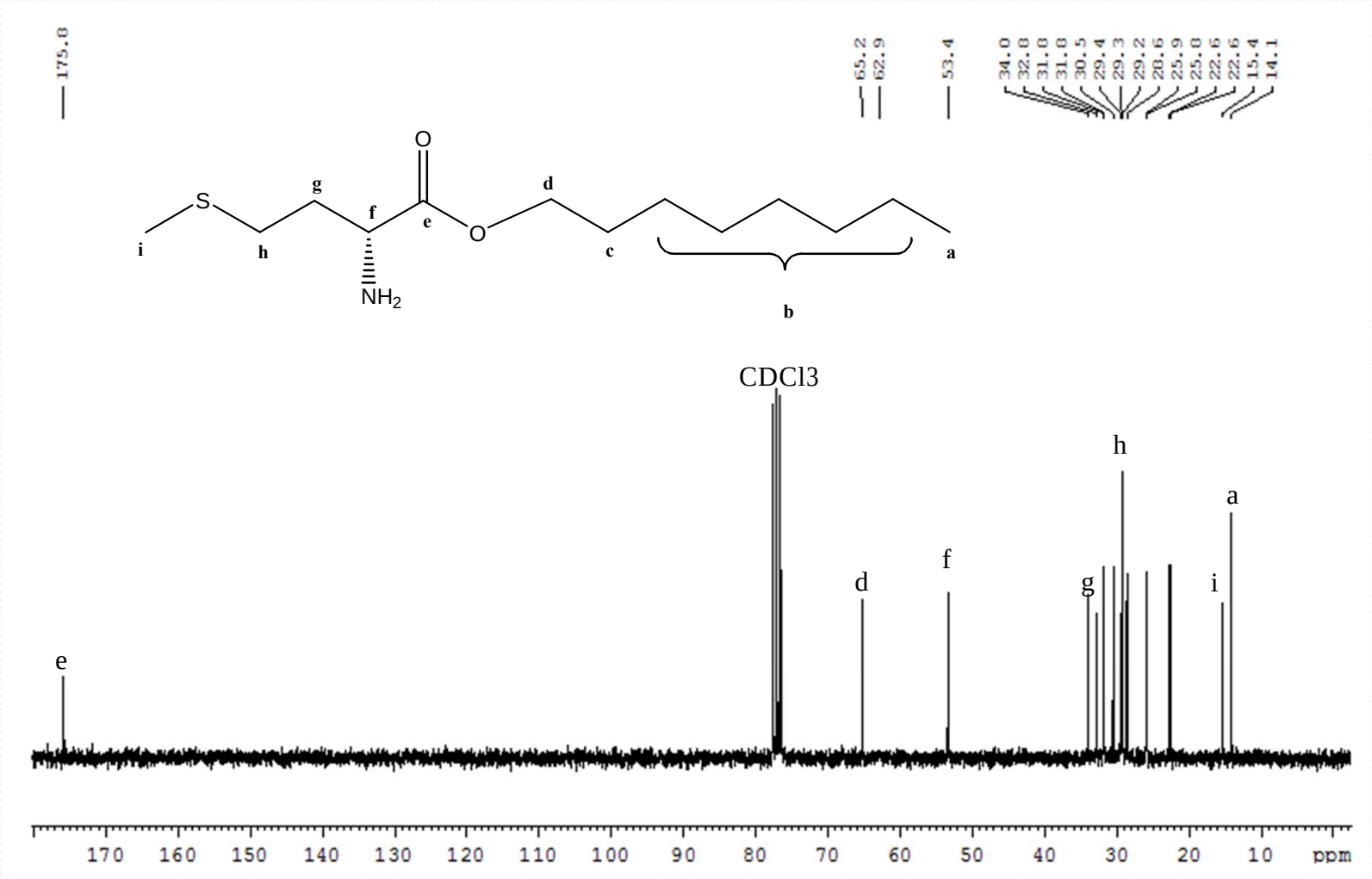
2a: n= 8; 2b: n=10; 2c: n=12

Chain length	Methionine esters	% Yield	Methionine ester hydrochloride	% Yield
8	1a	81	2a	70
10	1b	66	2b	62
12	1c	54	2c	50

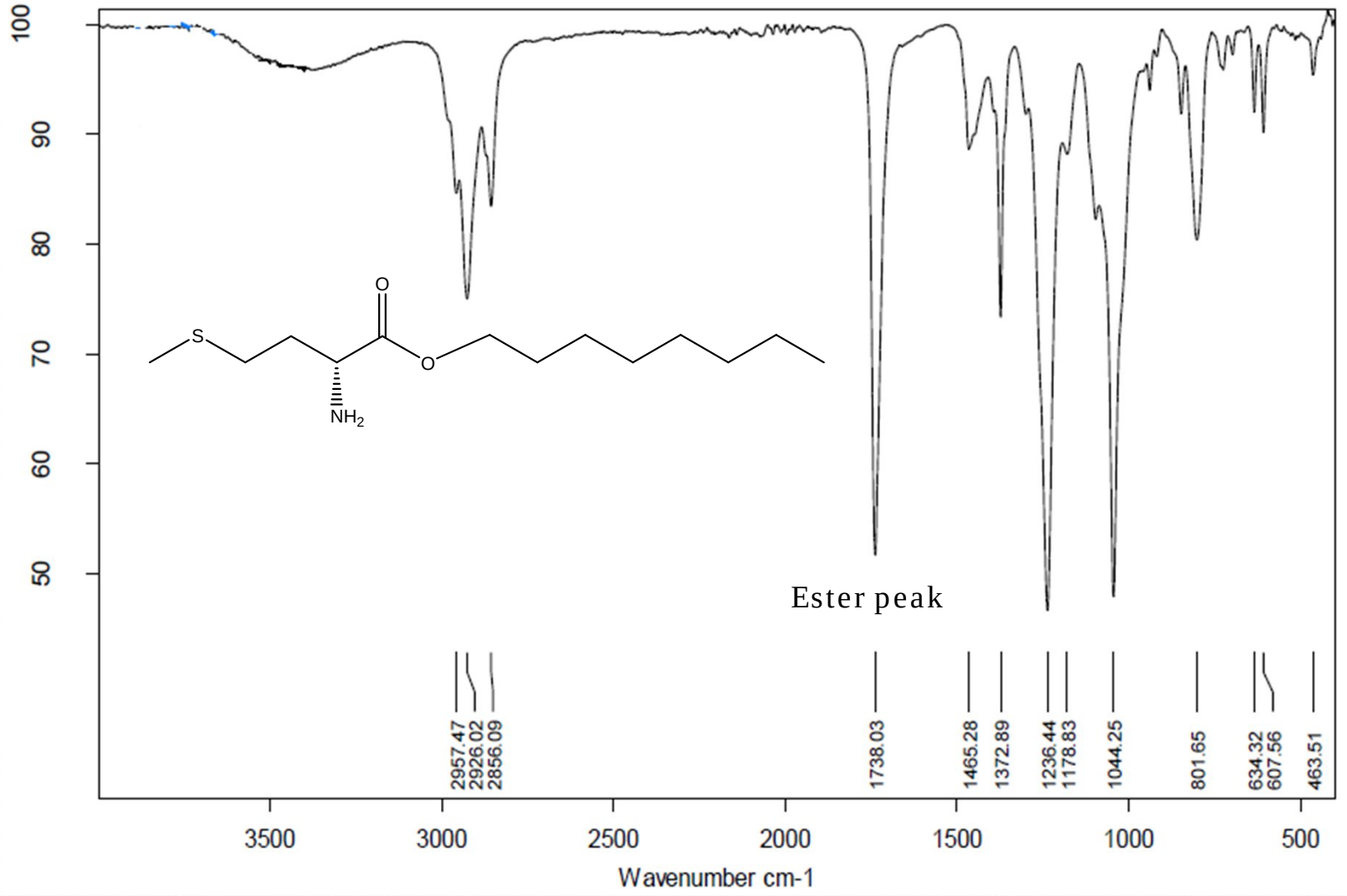
^{1}H NMR spectrum



^{13}C NMR spectrum

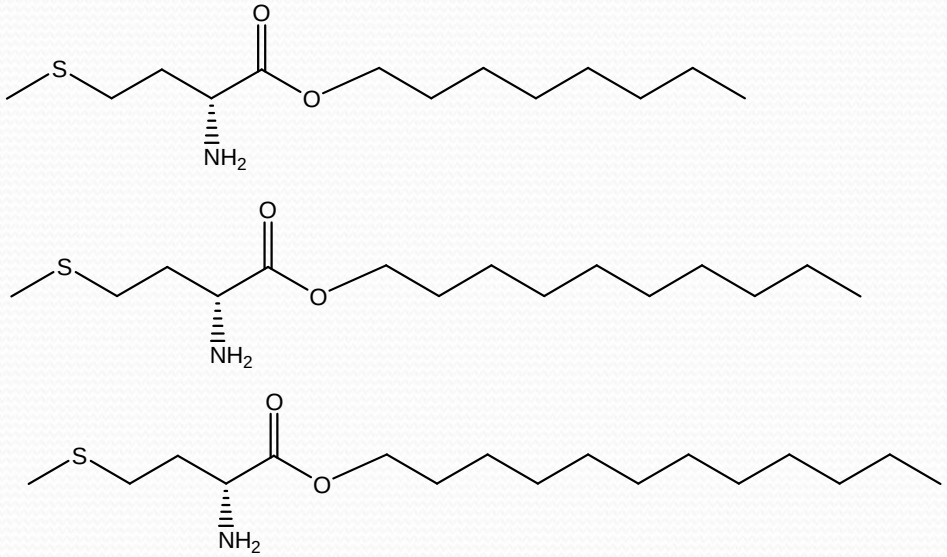


IR spectra

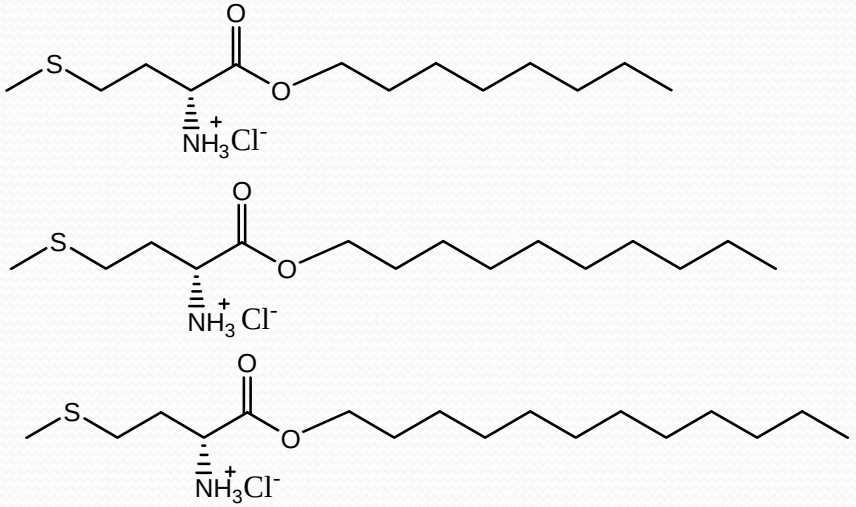

100
90
80
70
60
50
O
S
O
NH2
Ester peak
2957.47
2926.02
2856.09
1738.03
1465.28
1372.89
1236.44
1178.83
1044.25
801.65
634.32
607.56
463.51
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Synthesized compounds

Non-ionic surfactant
Methionine ester



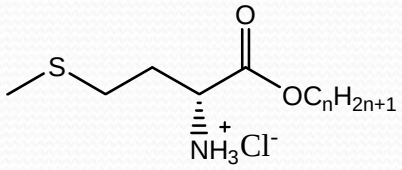
Cationic surfactant
Methionine ester hydrochloride

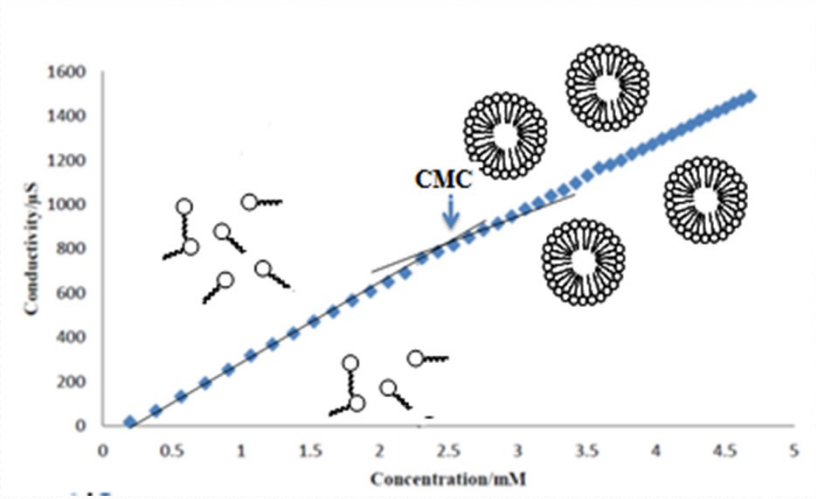


Physicochemical properties

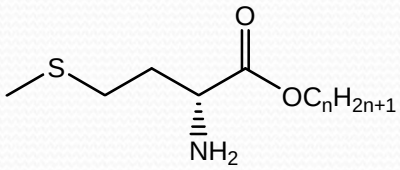
Critical micelle concentration

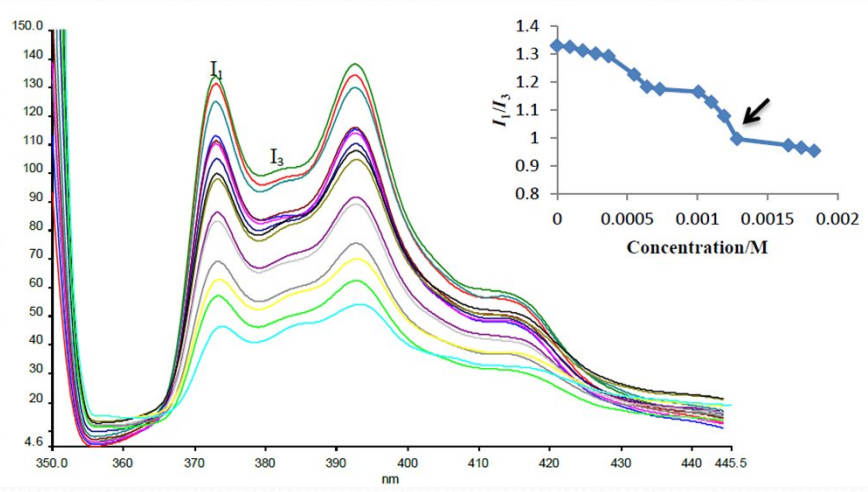
Conductivity measurements





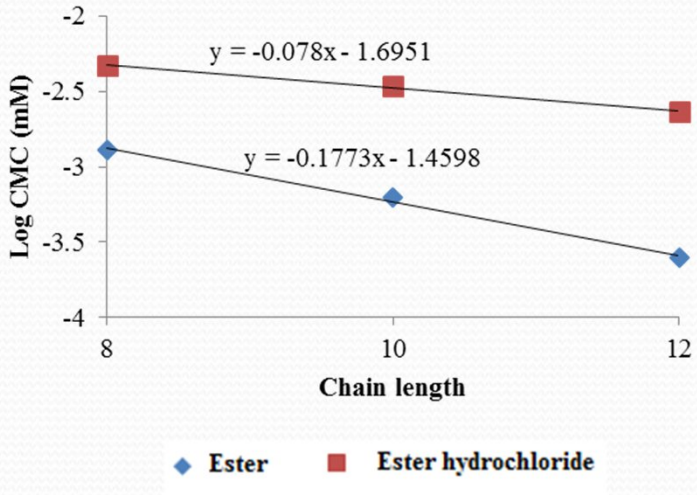
Pyrene fluorescence measurements





Comparing the CMC of the methionine esters with their ester hydrochloride derivatives

Chain length	Methionine esters	CMC (mM)	Methionine ester hydrochloride	CMC (mM)
8	1a	1.28	2a	4.74
10	1b	0.63	2b	3.42
12	1c	0.25	2c	2.31



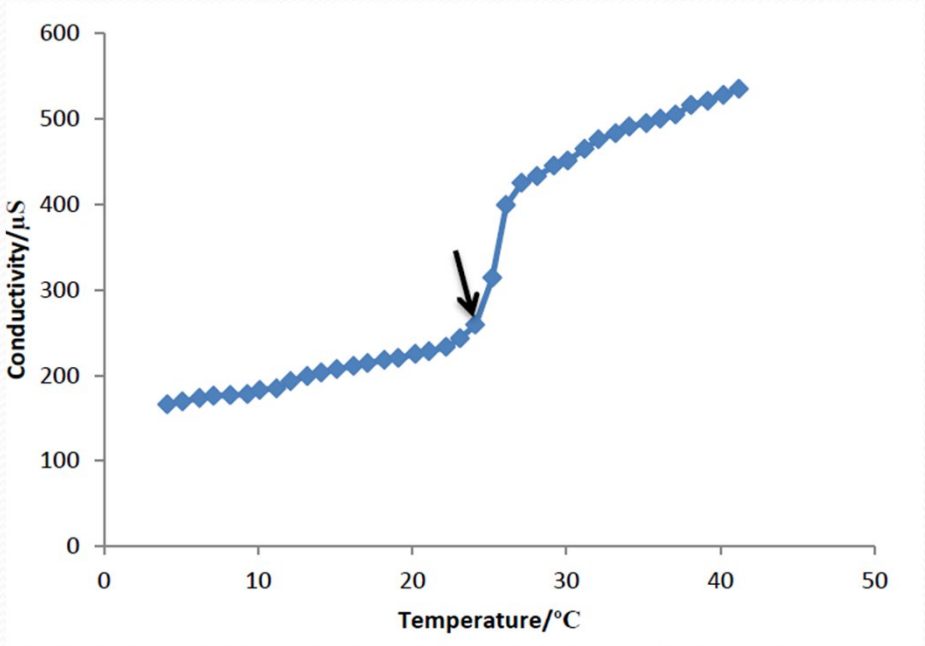
- In both series, the CMC was found to decrease with increasing chain length of the surfactants.
- The CMC of the methionine esters were lower than their corresponding ester hydrochloride derivatives.
- The ester hydrochlorides have less tendency to micellise due to repulsion between their cationic head groups

Physicochemical properties

The Krafft Temperature (T_K)

The minimum temperature at which surfactant can form micelles in aqueous solution

Obtained from the plot of conductivity of surfactant solution (above CMC) versus temperature



Effect of chain length on the Krafft temperature.

Methionine ester hydrochloride	Tk (°C)
2a	**23**
2b	**25**
2c	**29**
CTAB (cetyl trimethylammonium bromide)	**22**

The ester hydrochloride derivatives showed an increase in the Krafft temperature with increasing chain length showing that the surfactants with longer chain length has a tendency to micellise at a much higher temperature

Conclusion

- The methionine esters with varying chain lengths as well as their hydrochloride derivatives were successfully synthesized.
- The CMC of the methionine esters and their hydrochloride derivatives were found to decrease with chain length, as observed for previously reported surfactants.
- The methionine ester hydrochloride derivatives have a less tendency to micellise compared to their non-ionic ester derivatives due to the repulsion caused by their cationic head groups.
- An increase in chain length of the methionine ester hydrochloride caused an increase in the Krafft temperature of the surfactants, suggesting that the methionine surfactants with longer chain length micellise at higher temperatures