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Equilibrium and dynamic surface tension properties of Gemini quaternary ammonium salt surfactants with ester groups

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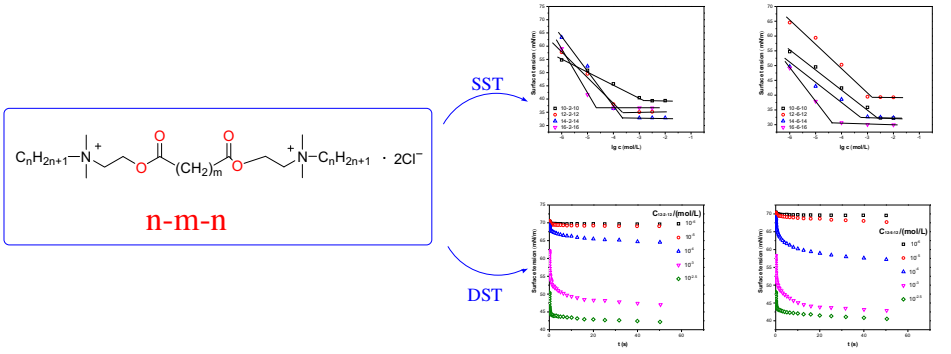
HIGHLIGHTS

- Eight gemini surfactants n-m-n (n = 10, 12, 14, 16; m = 2, 4) were synthesized.
- The cmc decreased with the an increase in chain length, increased with the length of spacer group.
- D_S, D_L decrease with increased concentration with constant n.
- Lengths of hydrophobic chain and sapcer group have no significant effect on D_S and D_L.

GRAPHICAL ABSTRACT



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ABSTRACT

Two series of quaternary ammonium salt Gemini surfactants with ester groups (n-m-n, where n represents hydrocarbon chain lengths of 10, 12, 14 and 16, m represents spacer group lengths of 2 and 6) were synthesized and characterized by ^{1}H NMR. Surface activity and adsorption of these cationic Gemini surfactants were investigated by methods of measuring equilibrium surface tension and dynamic surface tension. The critical micelle concentration (CMC) decreased with an increase in chain length, while increased with the length of spacer group. Moreover, data obtained were analyzed in accordance with Word-Tordai equation, and the diffusion coefficients for ionic liquid molecular adsorption in the initial stage and final stage under different concentration were figured out respectively. The results indicated that the adsorption process was controlled by a diffusion step at low surfactant concentration while by a mixed kinetic-diffusion adsorption mechanism at high surfactant concentration.

1. Introduction

Surfactants could change interface property significantly and their adherence to the interface results in decreased surface tension, which is the foundation for its widespread application in commodity chemicals, agrochemicals, oil exploration and food processing [1]. The formation of fresh interface is a dynamic process, properties of equilibrium and dynamic adsorption in the process of Gemini surfactants' transfering to the interface influence the function of surfactants. The spreading of pesticides, the formation of foam, the formation of emulsion and other rapid adsorption processes have been completed before surfactants adsorption reach equilibrium. For example, research on dynamic surface tension of emulsifier is necessary in order to satisfy the pesticide's demand

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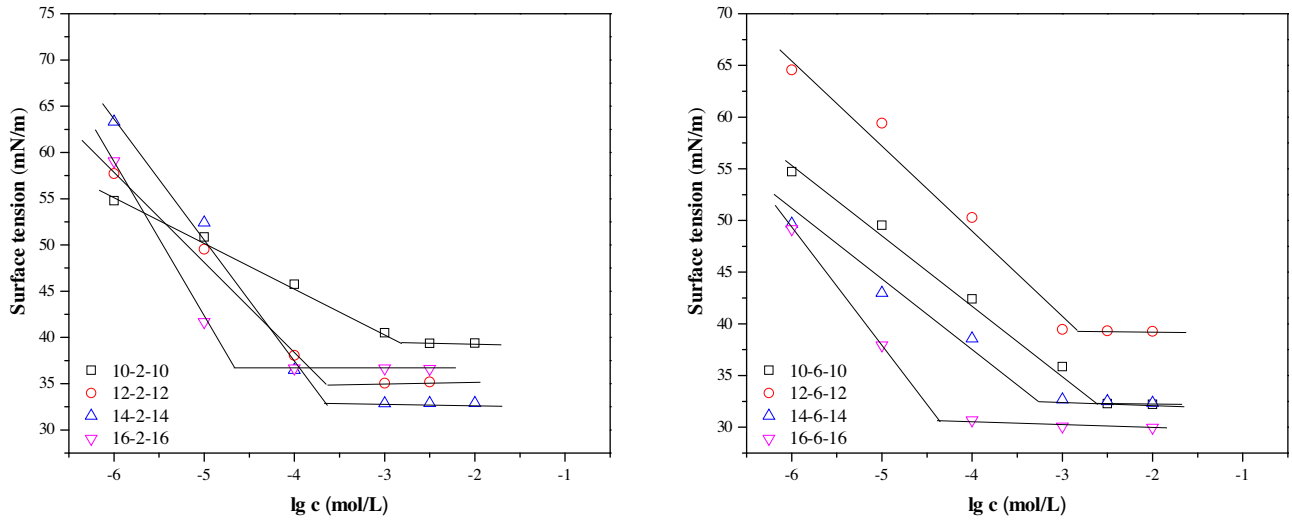

Fig. 1. Variation in the surface tension with the surfactant concentration for **n-m-n** at 25 °C.

Table 1
The synthesis of **n-m-n** series products.

n-2-n	yield (%)	n-6-n	yield (%)
10-2-10	32.61	10-6-10	30.09
12-2-12	54.38	12-6-12	42.03
14-2-14	67.32	14-6-14	61.81
16-2-16	60.08	16-6-16	59.69

of spreading on the leaf surface speedily [2]. In mineral extraction, the measure of froth flotation is also associated with the dynamic adsorption of surfactant [3]. Therefore, it can be predicted that further understanding of dynamic surface tension(DST)and the adsorption mechanism will contribute to the applications of surfactants in related frontiers.

Gemini surfactants containing two hydrophobic chains and two hydrophilic groups in one molecule have attracted more and more attention. The spacer group is a unique component in Gemini surfactant molecule, which strongly tightens the connection and reduces the electrostatic repulsion between the hydrophilic groups. Thus it is more probably for the alkly chain to generate more hydrophobic force. Those combined is the root cause of spacer group's superior properties in comparision with traditional single-headgroup and single-alkyl chain surfactants. Given this, it is possible to obtain different functional Gemini surfactants through changing its component [4], hydrophobic chain [5], spacer group length [6], spacer group softness [7] and introducing specific functional groups [8,9] depending on factual need. Those changes of factors enrich structure of and add superior function to Gemini surfactants. The environmental concerns and biodegradability issues have also influenced the chemist to design biocompatible surfactant molecules having ester functional group that can be easily degraded after use [10–12]. Bisquaternaryammoium salt gemini surfactant with ester bond, a new type of cationic surfactants, exhibits both high surface activities of the conventional surfactants

Table 2
Analysis of **n-2-n** ^{1}H NMR results.

10–2-10				**12–2-12**				**14–2-14**				**16–2-16**			
δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H
0.86–0.90	t	4.56	6	0.86–0.90	t	6.64	6	0.86–0.90	t	6.36	6	0.86–0.88	t	4.64	6
1,25–1,35	m	–	32	1.25–1.36	m	–	40	1.25–1.35	m	–	48	1.25–1.36	m	–	56
1.74–1.86	m	–	4	1.75	s	–	4	1.74	s	–	4	1.76	s	–	4
3.35–3.44	m	–	12	3.39–3.45	d	21.85	12	3.37–3.43	d	20.2	12	3.38–3.46	m	–	12
3.50–3.71	m	–	4	3.53–3.66	m	–	4	3.51–3.63	m	–	4	3.54–3.64	m	–	4
3.71	s	–	2	3.71–3.73	m	–	2	3.72	s	–	3	4.09–4.16	d	21.36	4
4.03–4.10	m	–	4	4.09–4.17	d	31.88	4	4.10	s	–	4	4.60–4.70	d	35.36	4
4.64–4.70	d	13.44	2	4.68	s	–	2	4.68	s	–	1				

Table 3
Analysis of **n-6-n** ^{1}H NMR results.

10–6-10				**12–6-12**				**14–6-14**				**16–6-16**			
δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H	δ(ppm)	Peak shape	*J* (Hz)	H
0.86–0.90	m	–	6	0.86–0.90	t	6.56	6	0.86–0.90	t	5.8	6	0.86–0.90	t	6.56	6
1.25–1.36	m	–	32	1.25–1.36	m	–	40	1.25	s	–	48	1.25–1.35	m	–	56
1.63	s	–	4	1.63	t	6,92	4	1.36	s	–	4	1.62–1.66	t	6.4	3
1.76	s	–	4	1.75	s	–	4	1.75	s	–	4	1.76–1.86	m	–	3
2.34–2.39	m	–	4	2.33–2.39	m	–	4	2.74	s	–	4	2.82	s	–	3
3.49	s	–	12	3.47	s	–	12	3.44	s	–	12	3.46–3,50	d	11.08	9
3.59–3.61	t	8.44	4	3.46–3.59	t	8.4	4	3.62	s	–	4	3.59–3.63	t	8.52	3
4.11	s	–	4	4.08	s	–	4	4.17	s	–	4	4.12	s	–	3
4.59	s	–	4	4.57	s	–	4	4.70	s	–	4	4.60	s	–	3