

Reactive surfactants in heterophase polymerisation XXIII. Synthesis and characterisation of novel dialkyl maleate cationic surfmers¹

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Abstract

A series of alkyl pyridinium bromide maleate diester surfmers were synthesised together with their saturated non-polymerisable succinate analogues. Each series consisted of four surfactants with the maleate or succinate function at different positions on the alkyl chain with the integrated length of the alkyl chain being more or less constant. The surface activity was evaluated and the critical micelle concentration (cmc) was found to be dramatically affected by the position of the maleate or succinate group. For the cases in which the pyridinium ring was close to the carboxylate group of the maleate or succinate, all the experimental observations could be explained if there was an interaction between the cationic N centre and the ester(s) reducing the charge density of the headgroup and, for example, allowing a closer packing of the molecules at the air–water interface. Overall, however, these species behaved similarly to conventional surfactants such as cetylpyridinium bromide. Those species in which the maleate or succinate group was placed in the terminal position of the hydrophobic tail showed abnormally high ($\sim \times 10$) critical micelle concentrations suggesting that the polar group in this position reduced considerably the overall hydrophobic nature of the surfactant tail. These molecules also appear to adopt a looped conformation at the air–water interface. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Surfactant monomers have generated much interest due to their dual nature, as surface active species and polymerisable monomers. In 1958 the syntheses of the first ‘vinyl soaps’ were reported [1]. Nowadays the more general term ‘surfmers’ is used, which derives from SURfactant monoMERS. As reactive monomers these materials have been used to synthesise entirely novel materials and to achieve polymerisation in structurally ordered media. They have also been used in heterogeneous polymerisations, e.g. emulsion polymerisations replacing conventional surfactants with the aim of improving latex properties.

To date, surfmers used in emulsion polymerisation have contained typically acrylic and methacrylic [2–4], acrylamido [5], and styrenic [6] polymerisable groups. It was found that such monomers are capable of producing water-soluble polyelectrolytes when used above their critical micelle concentration (cmc), which contributes to the coagulation of the latex. Less reactive functionalities such as allylic [7–9], and allyloxy [10,11], have also been used in emulsion polymerisation. However it was found that allyl surfmers decrease the polymerisation rate of the main monomer, and this was attributed to degenerative chain transfer reactions to the allyl function. Lately maleic acid derivatives have been proposed as the reactive species [12–15], since this kind of function can undergo copolymerisation with suitable comonomers, but cannot be homopolymerised. In emulsion polymerisation, mainly anionic [5–8,10,12,14] and non-ionic [3,11], amphiphiles have been used. Very little work has been done with cationic [4,15] and zwitterionic [16,17] species for this application, although recently phospholipids [16] have been used to mimic biomembranes in monodisperse latices. The relative

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positions of the three moieties present in a surfmer molecule, i.e. hydrophilic head, hydrophobic tail and polymerisable function, are not restricted, that is to say, the polymerisable group can be placed at the end of the hydrophobic tail [18], in the middle of the hydrophobe [13], attached to the hydrophilic head [19] or in the counter-ion [20]. In emulsion polymerisation mainly tail-type surfmers have been used which, in principle, seems to be most appropriate since the reactive function will be placed just below the surface of or within a particle facilitating participation in the polymerisation process. Ferguson et al. [3] studied nonionic head-type surfmers in emulsion polymerisation and found that they were not as efficient as tail-type. Similar results for tail-type surfmers have been reported [21].

The surface activity of these of amphiphiles can be affected significantly by the presence of the polymerisable group [4,18,22,23], which in turn may influence the final performance in emulsion polymerisation [23]. When the hydroxyl head of a nonionic surfmer is capped with an acrylate function, the cmc decreases relative to the uncapped non-polymerisable precursor. This behaviour indicates a decrease in the overall hydrophilicity of the molecule as a result of making the head group less hydrophilic [3].

In a large collaborative research programme [24] the most appropriate polymerisable function has been sought and it has been concluded that functions not capable of homopolymerising in the aqueous phase are probably the best, e.g. maleates. Consequently in the present study the synthesis of a series of structurally related dialkyl maleates was undertaken and their surface activity properties assessed. In the following paper their performance in emulsion polymerisation will be described [25].

2. Experimental

2.1. Materials

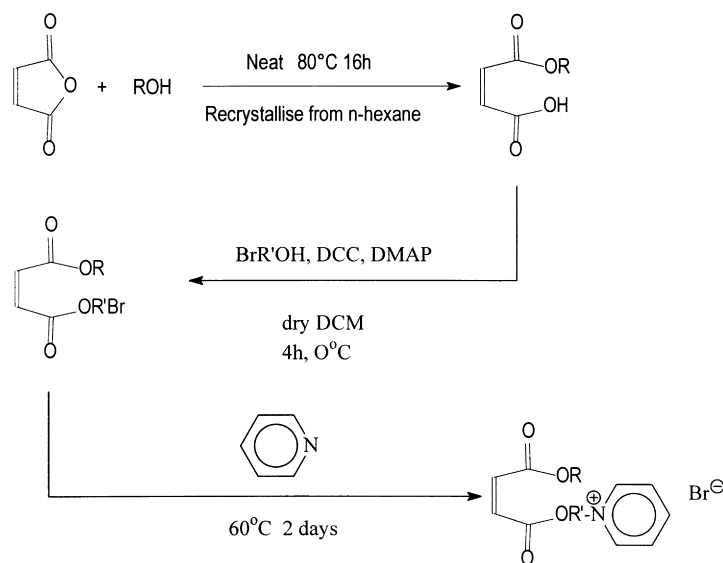
Maleic anhydride, succinic anhydride, dodecan-1-ol, decan-1-ol, hexan-1-ol, 11-bromoundecan-1-ol, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), bromoethanol, 6-bromohexan-1-ol, methanol and pyridine were obtained from Aldrich Chem. Co. Ltd. and used as received. Other reagents and solvents were general purpose species and were used as supplied unless specified otherwise in preparations.

2.2. Analytical equipment

^1H nuclear magnetic resonance (n.m.r.) spectra were obtained on a Bruker AMX250 instrument. The solvent peak was used as an internal standard. Elemental microanalyses were performed on a Perkin-Elmer Series II Elemental Analyser. Melting points were recorded using a Gallenkamp Digital Melting Point Apparatus.

2.3. Synthesis of alkyl maleic or succinic acid monoesters

These were prepared as shown in Scheme 1. A typical reaction is as follows. Maleic anhydride (20.0 g, 0.20 mol) and decan-1-ol (32.3 g, 0.20 mol) were placed in a 500 cm³ round-bottomed flask fitted with a reflux condenser. The latter was placed in an oil bath at 80°C for 20 h and was stirred magnetically. When a white solid product was obtained, it was recrystallised from *n*-hexane. Liquid products, however, were used without further purification. Experimental data for the other syntheses are given in Table 1. A summary of ^1H n.m.r. assignments and elemental microanalytical data for the products appear in Table 2.



Scheme 1. Synthesis of alkyl pyridinium bromide maleate diester surfmers.

Table 1
Preparation of alkyl maleic and succinic acid monoesters

Compound	Anhydride (g, mol)	Alcohol (g, mol)	Product (g, mol)	Yield (%)
brc11m	Maleic anhydride (5.0, 0.05)	11-Bromoundecan-1-ol (12.8, 0.05)	White solid 14.6(0.042)	80
c6m	Maleic anhydride (5.0, 0.05)	Hexan-1-ol (5.2, 0.05)	Clear liquid (9.2, 0.046)	90
c10m	Maleic anhydride (20.0, 0.20)	Decan-1-ol (32.3, 0.20)	White solid (43.1, 0.16)	80
c12m	Maleic anhydride (20.0, 0.20)	Dodecan-1-ol (38.0, 0.20)	White solid (48.7, 0.17)	80
brc11s	Succinic anhydride (1.0, 0.01)	11-Bromoundecan-1-ol (2.5, 0.01)	White solid (2.2, 0.0063)	60
c6s	Succinic anhydride (5.0, 0.05)	Hexan-1-ol (5.1, 0.05)	Clear liquid (9.9, 0.049)	90
c10s	Succinic anhydride (20.0, 0.2)	Decan-1-ol (31.6, 0.2)	White solid (40.2, 0.15)	70
c12s	Succinic anhydride (5.0, 0.05)	Dodecan-1-ol (9.3, 0.05)	White solid (11.7, 0.041)	80

2.4. Synthesis of alkyl bromoalkyl maleate or succinate diesters

These were prepared as shown in Scheme 1. A typical reaction is as follows. Decyl monoester maleic acid (**c10m**) (5.0 g, 19 mmol) was dissolved in dry dichloromethane

(DCM) (150 cm³) in a round-bottomed flask fitted with a drying tube and cooled to 0°C under magnetic stirring. Then, DCC (4.1 g, 0.019 mol), DMAP (0.5 g, 4.0 mmol) and bromoethanol (2.4 g, 0.02 mol) were added. The reaction was allowed to come to room temperature over 4 h. The resulting solution was filtered to remove the

Table 2
¹H n.m.r. assignments and elemental microanalytical data for the alkyl maleic and succinic acid monoesters

Compound	Formula	MW	Microanalytical data (%)						¹ H n.m.r. chemical shifts
			Expected			Found			
			C	H	Br	C	H	Br	
brc11m	C ₁₅ H ₂₅ O ₄ Br	349.23	51.6	7.2	22.9	51.3	7.0	22.6	(CDCl ₃): δ = 1.29–1.41 (m, 18H, –CH ₂ –), 1.83 (m, 2H, –CH ₂ –CH ₂ –CH ₂ –O–), 3.41 (t, 2H, –CH ₂ –Br, <i>J</i> = 5.7 Hz), 4.3 (t, 2H, –CH ₂ –OCO, <i>J</i> = 5.7 Hz), 6.43 (AA', 2H, –CH=CH–, <i>J</i> = 11.4 Hz), 10.5 (s, 1H, –COOH ^b)
c6m	C ₁₀ H ₁₆ O ₄	200.2	60.0	8.05		60.1	8.0		(CDCl ₃): δ = 0.83 (t, 3H, CH ₃ –, <i>J</i> = 5.7 Hz), 1.15–1.3 (m, 6H, –CH ₂ –), 1.65 (m, 2H, –CH ₂ –CH ₂ –CH ₂ –O–), 4.17 (t, 2H, –CH ₂ –OCO–, <i>J</i> = 5.7 Hz), 6.34 (m, 2H, –CH=CH–) ^a , 10.5 (s, 1H –COOH ^b)
c10m	C ₁₄ H ₂₄ O ₄	256.30	65.6	9.4		65.5	9.2		(CDCl ₃): δ = 0.88 (t, 3H, CH ₃ –, <i>J</i> = 4 Hz), 1.2–1.3 (m, 14H, –CH ₂ –), 1.62 (m, 2H, –CH ₂ –CH ₂ –CH ₂ –O–), 4.25 (t, 2H –CH ₂ –OCO–, <i>J</i> = 4 Hz), 6.40 (AA', 2H, –CH=CH–, <i>J</i> = 10.4 Hz), 10.3 (s(br), 1H, –COOH)
c12m	C ₁₆ H ₂₈ O ₄	284.36	67.6	9.9		67.1	9.5		(CDCl ₃): δ = 0.88 (t, 3H, CH ₃ –, <i>J</i> = 5 Hz), 1.26–1.33 (m, 19H, –CH ₂ –), 1.69 (m, 2H, –CH ₂ –CH ₂ –O–, <i>J</i> = 5 Hz), 4.28 (t, 2H, –CH ₂ –OCO–, <i>J</i> = 5 Hz), 6.43 (AA', 2H, –CH=CH–, <i>J</i> = 10.3 Hz), 10.5 (s, 1H, –COOH ^b)
brc11s	C ₁₅ H ₂₇ OBr	351.24	51.2	7.75	22.7	51.1	7.45	22.9	(CDCl ₃): δ = 1.3–1.4 (m, 18H, –CH ₂ –), 1.83 (m, 2H, –CH ₂ –CH ₂ –O–), 2.6 (m, 4H, –OCOCH ₂ –CH ₂ –OCO–), 3.41 (t, 2H, –CH ₂ –Br, <i>J</i> = 7 Hz), 4.1 (t, 2H, –CH ₂ –OCO–, <i>J</i> = 6.8 Hz), 10.5 (s, 1H, –COOH ^b)
c6s	C ₁₀ H ₁₈ O ₄	202.21	59.4	9.0		59.7	9.3		(CDCl ₃): δ = 0.83 (t, 3H CH ₃ –, <i>J</i> = 4.6 Hz), 1.15–1.63 (m, 6H, –CH ₂ –), 1.65 (m, 2H, –CH ₂ –CH ₂ –O–), 2.6 (m, 4H, –OCOCH ₂ –CH ₂ –OCO–), 4.17 (t, 2H, –CH ₂ –OCO–), <i>J</i> = 6.6 Hz), 10.5 (s, 2H, –COOH)
c10s	C ₁₄ H ₂₆ O ₄	258.32	65.1	10.1		65.6	9.6		(CDCl ₃): δ = 0.99 (t, 3H, CH ₃ –, <i>J</i> = 6.75 Hz), 1.2–1.69 (m, 16H, –CH ₂ –), 2.6 (m, 4H, –OCOCH ₂ –CH ₂ –OCO–), 3.9 (t, 2H, –CH ₂ –OCO–, <i>J</i> = 6.75 Hz) 10.5 (s, 1H, –COOH ^b)
c12s	C ₁₆ H ₃₀ O ₄	286.37	67.1	10.6		67.2	10.6		(CDCl ₃): δ = 0.88 (t, 3H, CH ₃ –, <i>J</i> = 5.6 Hz), 1.2–1.7 (m 20H, –CH ₂ –), 2.6 (m, 4H, –OCOCH ₂ –CH ₂ –OCO), 4.1 (t, 2H, –CH ₂ –OCO–, <i>J</i> = 6.7 Hz), 10.5 (s, 1H, –COOH ^b)

^aThis product was a liquid and the maleate resonances were not resolved.

^bBroad signal.

Table 3
Preparation of alkyl bromoalkyl maleate and succinate diesters

Compound	Alcohol (g, mol)	Acid (g, mol)	DCC (g, mol)	DMAP (g, mol)	Product (g, mol)	Yield (%)
c1mc11br	Methanol (0.4, 0.015)	brc11m (5.0, 0.015)	(2.9, 0.015)	(0.34, 2.8)	Yellow liquid (2.0, 0.0055)	40
c6mc6br	6-Bromohexan-1-ol (4.5, 0.024)	c6m (5.0, 0.024)	(5.2, 0.024)	(0.6, 4.9)	Yellow liquid (3.6, 0.0099)	40
c10mc2br	2-Bromoethan-1-ol (2.4, 0.019)	c10m (5.0, 0.020)	(4.1, 0.021)	(0.5, 3.9)	Yellow liquid (2.7, 0.0074)	38
c12mc2br	2-Bromoethan-1-ol (2.2, 0.17)	c12m (5.0, 0.17)	(3.7, 0.019)	(0.4, 3.5)	Yellow liquid (2.8, 0.0071)	41
c1sc11br	Methanol (0.4, 0.013)	BrC11s (4.6, 0.013)	(2.7, 0.014)	(0.3, 2.5)	Yellow liquid (3.4, 0.0093)	73
c6sc6br	6-Bromohexan-1-ol (1.8, 0.0099)	c6s (2.0, 0.099)	(2.0, 0.010)	(0.2, 1.9)	Yellow liquid (2.6, 0.0071)	74
c10sc2br	2-Bromoethan-1-ol (4.8, 0.038)	C10s (10.0, 0.039)	(7.9, 0.041)	(0.9, 7.6)	Yellow liquid (10.2, 0.028)	73
c12sc2br	2-Bromoethan-1-ol (2.2, 0.17)	C12s (5.0, 0.17)	(3.6, 0.017)	(0.4, 3.4)	Yellow liquid (4.1, 0.010)	62

dicyclohexylurea formed. The solution was then washed with HCl (10% aqueous solution, $2 \times 150 \text{ cm}^3$), and saturated NaHCO_3 solution ($2 \times 150 \text{ cm}^3$) and finally deionised water ($1 \times 150 \text{ cm}^3$). The organic layer was separated, dried over CaCl_2 , and the solvent removed. A brown viscous liquid was obtained (26.3 g). The desired product was separated from impurities by flash column chromatography, using silica as the stationary phase and a mixture of DCM and petroleum ether 40–60° (80:20) as eluent. Experimental data for the

other syntheses are summarised in Table 3, while Table 4 contains the ^1H n.m.r. assignments and the corresponding elemental microanalytical data for the products.

2.5. Synthesis of alkyl pyridinium bromide maleate or succinate diester surfactants

These were prepared as shown in Scheme 1. A typical reaction is as follows. Bromoethyl decyl maleate

Table 4
 ^1H n.m.r. assignments and elemental microanalytical data for the alkyl bromoalkyl maleate and succinate diesters

Compound	Formula	MW	Microanalytical data (%)						^1H n.m.r. chemical shifts
			Expected			Found			
			C	H	Br	C	H	Br	
c1mc11br	$\text{C}_{16}\text{H}_{27}\text{O}_4\text{Br}$	363.25	52.9	6.95	20.5	53.5	7.6	22.6	(CDCl_3): $\delta = 1.3\text{--}1.83$ (m, 18H, $-\text{CH}_2-$), 3.41 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.75$ Hz), 3.81 (s, 3H, $\text{O}-\text{CH}_3$), 4.18 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 6.7$ Hz), 6.65 (s, 2H, $-\text{CH}=\text{CH}-$)
c6mc6br	$\text{C}_{16}\text{H}_{27}\text{O}_4\text{Br}$	363.25	52.9	6.95	20.5	53.4	7.65	21.8	(CDCl_3): $\delta = 0.88$ (t, 3H, CH_3 , $J = 5.7$ Hz), 1.4–1.91 (m, 16H, $-\text{CH}_2-$), 3.41 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.0$ Hz), 4.18 (m, 4H, $-\text{CH}_2-\text{OCO}-$), 6.58 (s, 2H, $-\text{CH}=\text{CH}-$)
c10mc2br	$\text{C}_{16}\text{H}_{27}\text{O}_4\text{Br}$	363.25	52.9	6.95	20.5	53.4	7.5	22.0	(CDCl_3): $\delta = 0.87$ (t, 3H, CH_3 , $J = 6$ Hz), 1.2–1.68 (m, 14H, $-\text{CH}_2-$), 3.56 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 7.5$ Hz), 4.19 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 6.6$ Hz), 4.51 (t, 2H, $\text{O}-\text{CH}_2-\text{CH}_2\text{Br}$, $J = 6.1$ Hz), 6.68 (s, 2H, $-\text{CH}=\text{CH}-$)
c12mc2br	$\text{C}_{18}\text{H}_{31}\text{O}_4\text{Br}$	391.3	55.2	8.0	20.4	54.1	8.0	19.2	(CDCl_3): $\delta = 0.88$ (t, 3H, CH_3 , $J = 7.0$ Hz), 1.2–1.67 (m, 20H, $-\text{CH}_2-$), 3.56 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6$ Hz), 4.20 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 7$ Hz), 4.52 (t, 2H, $\text{O}-\text{CH}_2-\text{CH}_2\text{Br}$, $J = 5$ Hz), 6.69 (s, 2H, $-\text{CH}=\text{CH}-$)
c1sc11br	$\text{C}_{16}\text{H}_{29}\text{O}_4\text{Br}$	365.27	52.6	8.0	21.8	52.3	8.0	22.3	(CDCl_3): $\delta = 1.3\text{--}1.83$ (m, 18H, $-\text{CH}_2-$), 2.8 (s, 4H, $-\text{OCOCH}_2-\text{CH}_2-\text{OCO}-$), 3.41 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.2$ Hz), 3.7 (s, 3H, $-\text{CH}_3$), 4.12 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 6.5$ Hz)
c6sc6br	$\text{C}_{16}\text{H}_{29}\text{O}_4\text{Br}$	365.27	52.6	8.0	21.8	53.4	8.0	21.6	(CDCl_3): $\delta = 1.30$ (t, 3H, CH_3 , $J = 6.5$ Hz), 1.4–2.1 (m, 16H, $-\text{CH}_2-$), 2.8 (s, 4H, $-\text{OCOCH}_2-\text{CH}_2-\text{OCO}-$), 3.52 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.5$ Hz) 4.29 (m, 4H, $-\text{CH}_2-\text{OCO}-$)
c10sc2br	$\text{C}_{16}\text{H}_{29}\text{O}_4\text{Br}$	365.27	52.6	8.0	21.8	52.1	7.7	21.9	(CDCl_3): $\delta = 0.88$ (t, 3H, CH_3 , $J = 6.5$ Hz), 1.2–1.3 (m, 14H, $-\text{CH}_2-$), 1.69 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.8 (m, 4H, $-\text{OCOCH}_2-\text{CH}_2-\text{OCO}-$), 3.50 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.2$ Hz), 4.06 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 6.5$ Hz), 4.42 (t, 2H, $\text{O}-\text{CH}_2-\text{CH}_2\text{Br}$, $J = 6.4$ Hz)
c12sc2br	$\text{C}_{18}\text{H}_{33}\text{O}_4\text{Br}$	393.82	54.9	8.45	20.3	55.0	8.7	20.6	(CDCl_3): $\delta = 0.88$ (t, 3H, CH_3 , $J = 6.2$ Hz), 1.1–1.64 (m, 20H, $-\text{CH}_2-$), 2.6 (m, 4H, $-\text{OCOCH}_2-\text{CH}_2-\text{OCO}-$), 3.50 (t, 2H, $-\text{CH}_2-\text{Br}$, $J = 6.2$ Hz), 4.08 (t, 2H, $-\text{CH}_2-\text{OCO}-$, $J = 6.5$ Hz), 4.49 (t, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{Br}$, $J = 6.5$ Hz)

Table 5
Preparation of alkyl pyridinium bromide maleate and succinate diester surfmers

Compound	Bromide (g, mmol)	Pyridine (g, mmol)	Product (g, mmol)	Yield (%)
c1mc11	C1mc11br (1.8, 5.1)	(2.0, 25)	Light brown solid (2.1, 4.7)	94
c6mc6	C6mc6br (1.6, 4.5)	(1.8, 22)	Light brown solid (1.3, 2.9)	67
c10mc2	C10mc2br (2.5, 6.8)	(2.7, 34)	Light brown solid (2.7, 6.1)	91
c12mc2	C12mc2br (2.5, 6.5)	(2.6, 32)	Light brown solid (2.6, 5.5)	84
c1sc11	C1sc11br (1.5, 4.2)	(0.6, 7.6)	Cream-white solid (1.5, 3.4)	82
c6sc6	C6sc6br (1.3, 3.5)	(0.6, 7.6)	Brown oil (1.0, 2.3)	64
c10sc2	C10sc2br (1.1, 3.1)	(0.5, 6.3)	Brown oil (0.4, 0.9)	33
c12sc2	C12sc2br (1.1, 2.5)	(0.4, 5.1)	Brown oil (0.3, 0.63)	29

(**c10mc2br**) (2.5 g, 6.8 mmol) and pyridine (2.7 g, 0.034 mol) were mixed together in a round-bottomed flask fitted with a condenser and a magnetic stirrer. After the first 40 h reaction at 60°C some precipitate started to appear. After 4 days the reaction was stopped and diethyl ether was added in order to precipitate the remainder of the product, which appeared as a light-brown solid in the case of the maleate esters. The succinate-based surfactants, however, were all oils except for **c11sc1**. Experimental data for the other syntheses are given in Table 5. A summary of ¹H n.m.r. assignments and elemental microanalytical data for all the products appear in Table 6.

2.6. Determination of solubility

The solubility of surfmers was estimated qualitatively by placing approximately 20 mg of material in a test tube and adding ca. 1 cm³ of solvent. Solubilisation or lack of it was assessed visually both at room temperature and on heating by means of a hot air gun.

2.7. Determination of Krafft temperature

Krafft temperatures were determined using a microscope (Olympus Vanox) equipped with a hot stage (Linkam TH600 hot-stage and a Linkam PR600 thermal controller). The onset of the solubility of a little crystal of surfactant suspended in water was taken as the Krafft temperature.

2.8. Determination of cmc

Surface tensions of surfactant solutions were measured at 25°C using the Du Nuoy ring method [26] employing a tensiometer supplied by White Electrical Instruments Co. Ltd. The instrument was calibrated using pure solvents of known surface tension [27]. Details of our own particular methodology are documented elsewhere [19].

3. Results and discussion

3.1. Synthesis of surfactants

Two series of cationic surfactants were synthesised, the structures of which are shown in Fig. 1. The hydrophilic

head group was chosen to be a pyridinium bromide, while the hydrophobic tail was a hydrocarbon chain with a maleate or succinate moiety in different positions.

The nomenclature chosen for these molecules is the following; monoesters are named by indicating the length of the alkyl chain and the corresponding acid moiety, an 'm' is used for maleic acid and an 's' for succinic acid derivatives, so maleic acid decanyl monoester is termed **c10m**. When the maleic anhydride is opened with 11-bromoundecan-1-ol (see later) the resulting monoester is named **brc11m**. Diesters are named by describing the length of the alkyl chain on both sides of the maleate or succinate moiety, indicating which of the alkyl chain terminates in the bromide. Thus, methyl 11-bromoundecanyl succinate is represented by **c1sc11br**. Finally, pyridinium salts (Fig. 1) are named using just the alkyl chain length on either side of the maleic or succinic moieties, the first alkyl chain being the one further away from the head group, and the second alkyl chain the one to which the pyridinium bromide is attached; for instance, dodecanyl 2-pyridinium ethyl maleate bromide is termed **c12mc2**.

These compounds were synthesised by initially attaching the hydrophobic tail to the copolymerisable function and finally attaching the hydrophilic head group. In the first step (Scheme 1) the hemiester of maleic or succinic acid was produced by opening of the corresponding anhydride with an alcohol. When the opening was accomplished with long-chain alcohols, pure solids were obtained; however, when methanol was used under the same conditions, the products were liquids which were more difficult to purify. Therefore, in the case of the synthesis of **c1mc11** and **c1sc11**, the initial opening of the maleic or succinic anhydride was carried out with bromoundecanol and the second esterification was carried out with methanol. In all cases yields of monoesters were good (Table 1, 60%–90%), likewise the analytical data (Table 2).

Since one of the main interests of this study was to assess the effect of the position of the maleate function in a range of surfmers, it was crucial that the second esterification proceeded without transesterification of the first ester or indeed hydrolysis of the latter. The most appropriate synthetic pathway was found to be the use of DCC as a dehydrating agent (Scheme 1). During this reaction dicyclohexylurea, DCU, is formed and slowly precipitates out of

Table 6
¹H n.m.r. assignments and elemental microanalytical data for alkyl pyridinium bromide maleate and succinate diester surfactants

Compound	Formula	MW	Microanalytical data (%)										¹ H n.m.r. chemical shifts
			Expected					Found					
			C	H	N	Br		C	H	N	Br		
clmc11	C ₂₁ H ₃₂ O ₄ NBr	442.35	57.0	7.3	3.2	3.2	18.1	57.8	7.7	3.2	18.8	(CDCl ₃): δ = 1.2–1.3 (m, 14H, -CH ₂ -), 1.69 (m, 2H, -CH ₂ -CH ₂ -O-), 3.81 (s, 3H, CH ₃ -O-), 4.15 (t, 2H, -CH ₂ -OCO-, J = 6.6 Hz), 5.08 (t, 2H, -CH ₂ -N ⁺ -, J = 5 Hz), 6.8 (s, 2H, -CH=CH-), 8.13 (t, 2H, pyr-H3/H5, J = 6.7 Hz), 8.51 (t, 1H, pyr-H4, J = 7.3 Hz) 9.6 (d, 2H, pyr-H2/H6, J = 5.5 Hz)	
clmc6	C ₂₁ H ₃₂ O ₄ NBr	442.35	57.0	7.3	3.2	18.1	55.9	7.7	3.1	18.6	(CDCl ₃): δ = 0.89 (t, 3H, CH ₃ -, J = 6.5 Hz), 1.3–1.7 (m, 18H, -CH ₂ -), 4.15 (m, 4H, -CH ₂ -OCO-), 5.08 (t, 2H, -CH ₂ -N ⁺ -, J = 7.5 Hz), 6.62 (s, 2H, -CH=C-H-), 8.13 (t, 2H, pyr-H3/H5, J = 6.6 Hz), 8.51 (t, 1H, pyr-H4, J = 7.4 Hz), 9.56 (d, 2H, pyr-H2/H6, J = 6.5 Hz)		
clmc2	C ₂₁ H ₃₂ O ₄ NBr	442.35	57.0	7.3	3.2	18.1	56.5	7.2	3.2	18.5	(CDCl ₃): δ = 0.88 (t, 3H, -CH ₃ -, J = 6.3 Hz), 1.2–1.3 (m, 14H, -CH ₂ -), 1.66 (m, 2H, -CH ₂ -CH ₂ -O-), 4.15 (t, 2H, -CH ₂ -OCO-, J = 6.7 Hz), 4.8 (t(br), 2H, O-CH ₂ -CH ₂ N ⁺ -), 5.6 (t(br), 2H, -CH ₂ -N ⁺ -), 6.63 (AA' 2H, -CH=CH-, J = 12.5), 8.13 (t, 2H, pyr-H3/H5, J = 6.7 Hz), 8.55 (t, 1H, pyr-H4, J = 7.6 Hz), 9.6 (d, 2H, pyr-H2/H6, J = 6.0 Hz)		
clmc2	C ₂₃ H ₃₆ O ₄ NBr	470.4	58.7	7.7	2.9	16.9	57.9	7.9	2.9	16.8	(CDCl ₃): δ = 0.88 (t, 3H, CH ₃ -, J = 6.7 Hz) 1.9–1.69 (m, 20H, -CH ₂ -), 4.17 (t, 2H, -CH ₂ -OCO-, J = 6.7 Hz), 4.8 (t, 2H, O-CH ₂ -CH ₂ N ⁺ -, J = 4.7 Hz), 5.58 (t, 2H, -CH ₂ -N ⁺ -, J = 4.7 Hz), 6.6 (AA' 2H, -CH=CH-, J = 12.0), 8.14 (t, 2H, pyr-H3/H5, J = 7.5 Hz), 8.55 (t, 1H, Pyr-H4, J = 7.5 Hz), 9.6 (d, 2H, pyr-H2/H6, J = 5.4 Hz)		
clsc11	C ₂₁ H ₃₄ O ₄ NBr	444.36	56.7	7.7	3.15	18.0	55.7	8.1	2.95	17.7	(CD ₃ OD): δ = 1.2–1.69 (m, 12H, -CH ₂ -), 2.55 (s, 4H, -OCOCH ₂ -CH ₂ -OCO-), 3.65 (s, 3H, CH ₃ -), 4.15 (t, 2H, -CH ₂ -OCO, J = 6.5 Hz), 4.6 (t, 2H, -CH ₂ -N ⁺ -, J = 6.5 Hz), 8.13 (t, 2H, pyr-H3/H5, J = 7 Hz), 8.6 (t, 1H, pyr-H4, J = 7.8 Hz), 9.6 (d, 2H, pyr-H2/H6, J = 5.4 Hz)		
clsc6	C ₂₁ H ₃₄ O ₄ NBr	444.36	56.7	7.7	3.15	18.0	56.4	8.1	2.6	18.2	(CD ₃ OD): δ = 0.88 (t, 3H, CH ₃ -, J = 6.5 Hz), 1.3–2.4 (m, 18H, -CH ₂ -), 2.6 (s, 4H, -OCOCH ₂ -CH ₂ -OCO), 4.15 (m, 8H, -CH ₂ -OCO), 4.8 (t, 2H, -CH ₂ -N ⁺ -, J = 7.1 Hz), 8.13 (t, 2H, pyr-H3/H5, J = 6.8 Hz), 8.6 (t, 1H, pyr-H4, J = 7.8 Hz), 9.2 (d, 2H, pyr-H2/H6, J = 6.1 Hz)		
clsc2	C ₂₁ H ₃₄ O ₄ NBr	444.36	56.7	7.7	3.15	18.0	57.5	7.3	3.8	22.3	(CD ₃ OD): δ = 0.88 (t, 3H, CH ₃ -, J = 6.8 Hz), 1.2–1.6 (m, 16H, -CH ₂ -), 2.6 (m, 4H, -OCOCH ₂ -CH ₂ -OCO), 4.10 (t, 2H, -CH ₂ -OCO-, J = 6.6 Hz), 4.7 (t, 2H, -O-CH ₂ -CH ₂ N ⁺ -, J = 5.8 Hz), 5.1 (t, 2H, -CH ₂ -N ⁺ -, J = 5.8 Hz), 8.13 (t, 4H, pyr-H3/H5, J = 6.8 Hz), 8.6 (t, 1H, pyr-H4, J = 7.8 Hz), 9.2 (d, 2H, pyr-H2/H6, J = 6.0 Hz)		
clsc2	C ₂₃ H ₃₈ O ₄ OBr	472.41	58.5	7.95	2.95	16.9	53.2	7.7	3.4	17.2	(CDCl ₃): δ = 0.88 (t, 3H, CH ₃ -, J = 6.4 Hz), 1.2–1.7 (m, 20H, -CH ₂ -), 2.6 (m, 4H, -OCOCH ₂ -CH ₂ -OCO), 4.15 (t, 2H, -CH ₂ -OCO-, J = 7.0 Hz), 4.7 (t, 2H, -O-CH ₂ -CH ₂ N ⁺ -, J = 5 Hz), 5.32 (t, 2H, -CH ₂ -N ⁺ -, J = 5.2 Hz), 8.13 (t, 4H, pyr-H3/H5, J = 6.7 Hz), 8.55 (t, 1H, pyr-H4, J = 7.8 Hz), 9.6 (d, 2H, pyr-H2/H6, J = 6 Hz)		

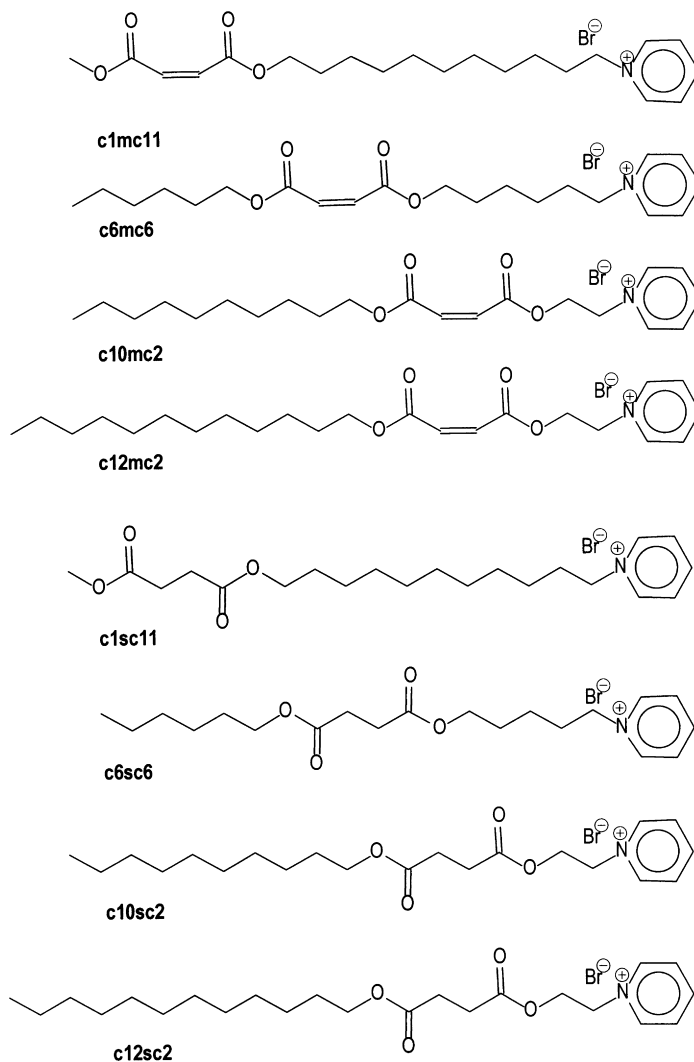


Fig. 1. Maleate and succinate series of pyridinium bromide surfactants.

solution. In the case of the succinates, DCU was recovered typically in over 95% yield; however, in the case of the maleates typically only 60% of the DCU was obtained. In addition, the yields of the maleate diester are consistently lower (38%–41%) than those of the succinate diesters (62%–74%) (Table 3). Hence it is thought that some side reaction occurs probably between the maleate acid and the DCC; however, to date the resulting products have not been identified and more effort is needed to understand this side reaction. In the last step of the synthesis (Scheme 1) pyridine is quaternised with the maleate or succinate alkyl bromide species. The succinate pyridinium salts were obtained in lower yields (29%–82%) than the corresponding maleate ones (67%–94%). The main reason for this was the less efficient work-up and recovery of the succinate species which are generally oily in nature. The analytical data (Table 6) for the succinate species are also somewhat poorer than those for the maleates (e.g. **c12sc2**), and again this is a reflection of the oily nature of these salts. However, surface tension data (see later) did not indicate any minima

around the critical micelle concentrations—an effect that is often indicative of low surfactant purity.

The raw ^1H n.m.r. spectra for the maleate series are shown in Fig. 2. It can be observed that the signals for the protons in the pyridinium ring are very similar in all cases and correspond to the expected ones. The signals appearing in the region from 4 to 6 ppm are assigned to protons A, C and D. In the case of **c1mc11** A protons (i.e. CH_3) appear as a singlet since they are not coupled to any other. In order to decide which triplet corresponds to protons C and D, the spectrum of **c6mc6** was used. In this case the methylenes attached to the two esters, i.e. A and C, are essentially equivalent, and therefore the integration of this signal will be double that corresponding to protons D. Hence the signal for the D protons is more downfield than that of the A, C protons as expected. From this the interpretation of the spectrum of **c1mc11** becomes clearer, and the triplet at ca. 4 ppm can be assigned to protons C, and that more downfield at 5.4 ppm to D protons. However, in the case of **c10mc2** and **c12mc2** the spectra look somewhat different

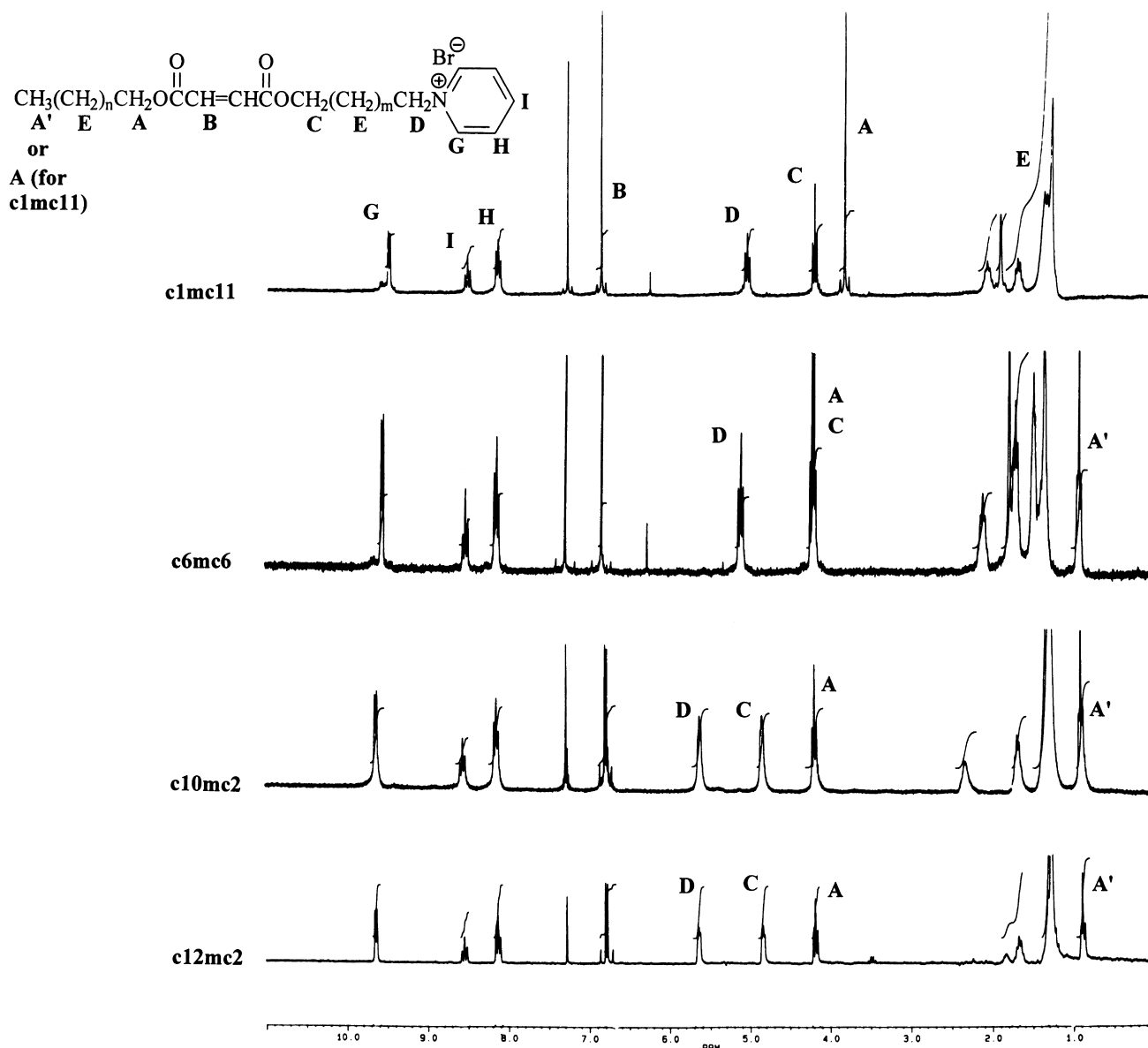


Fig. 2. ¹H n.m.r. spectra of alkyl pyridinium maleate diester surfmers.

from the previous two. Three triplets would be expected from protons A, C and D; however, only one sharp triplet is observed, the other two being rather broad peaks. The sharp triplet was initially assigned to protons A, since they resemble the C protons in the previous two spectra. The question is, however, why the other two signals appear as broad resonances and why their chemical shifts are somewhat different to those of related protons in the previous compounds. Firstly, there is an absence of E protons ($m = 0$) in **c10mc2** and **c12mc2**, and clearly *both* C and D protons are influenced significantly by *both* the flanking $-\text{CO}_2-$ and Py^{\oplus} groups. Not surprisingly therefore the C and D resonances appear downfield of the analogous protons in **c1mc11** and **c6mc6**. In addition, as will be postulated later, there is strong evidence for a direct interaction between the ester group adjacent to the C

methylene and the pyridinium ring, and therefore the mobility of the C protons will be considerably decreased and the signal consequently broadened. Likewise, broadening of the resonance of the D protons would not be surprising if such an interaction occurs. Spectra for succinate surfactants (not reproduced here) show similar characteristics.

The spectrum of **c1mc11** and **c6mc6** both show a small sharp resonance at ~ 6.3 ppm and the most likely source of this is a trace of maleate (possibly pyridinium) salt. This might arise from hydrolysis of the maleate diesters although it is not clear why this is manifest only in **c1mc11** and **c6mc6**. The resonance at ~ 7.3 ppm in the spectrum of **c10mc2** also appears to have some small extra peaks. A possible source for this might be a trace of fumarate ester arising from isomerisation, but the feature seems rather too downfield for this.

3.2. Solubility and Krafft temperature

It was observed that all amphiphiles are soluble in solvents such as methanol, ethanol and chloroform. Surfmers **c10mc2** and **c12mc2** are not soluble in acetone, similarly to cetylpyridinium bromide (CPB), whilst the rest are soluble. Interestingly, these two surfmers are those with the maleate function closer to the headgroup making interaction with, and solubilisation by, an aprotic polar solvent much more difficult. This contrasts with the behaviour of **c1mc11** and **c6mc6** which have the maleate function along the tail, making the interaction with acetone more favourable thus aiding solubilisation. All amphiphiles were insoluble in apolar hydrocarbon solvents as expected for cationic species [4]. Overall the succinates are found to have a wider solubility than the maleates.

The Krafft temperature, T_k , is the lower temperature limit for micellar properties of surfactants and is defined as the temperature at which the solubility/temperature curve meets the critical micelle concentration/temperature curve. Hence, for good micellar performance, low values of T_k are desirable. In cold water, the maleates were not soluble, in contrast to the succinates that were soluble at all temperatures. In the maleate series, **c10mc2** and **c12mc2** had a T_k above room temperature, 24 and 34°C, respectively, whereas for **c1mc1** and **c6mc6** T_k was 16°C (Table 7). Succinates were highly soluble above 15°C. At temperatures above 35°C all surfactants were soluble in water and foamed readily.

3.3. Melting points

From the structure of these surfactants, one might have expected **c10mc2** and **c12mc2** to have higher melting points since the hydrophobic tail is 'undisrupted' by the maleate function, making the packing within the ionic lattice and the interactions between the tails more efficient. However this was not the case. Surfmers **c10mc2** and **c12mc2** showed lower melting points than those displayed by **c1mc11** and **c6mc6**. The difference in structure between these two groups is simply the distance between the headgroup and the maleate function. Lower melting points in ionic

compounds may indicate a lower charge density of the molecules in the lattice. As a consequence, the electrostatic energy between molecules would be lower, as would the melting point. In the case of the maleate series all of the molecules had an identical ionic headgroup and therefore any difference in interactions had to be attributed to other factors. For **c10mc2** and **c12mc2** the short spacer group between the maleate group and the pyridinium cation might allow delocalisation of the positive charge via a favourable six-membered ring structure as indicated in Fig. 3. This would reduce the charge density in these molecules and consequently the melting points would be lower. For the **c1mc11** and **c6mc6** surfmers, the spacer group is too long to allow this specific interaction. Interaction between positively charged nitrogen atoms and ester oxygen atoms in similar molecules have been reported previously [28]. If **c10mc2** and **c12mc2** are compared, their melting points are very close, the higher being that corresponding to the amphiphile with the longer hydrocarbon chain.

All the maleate surfmers were obtained as light-brown powders, whilst the succinates were all oily compounds with the exception of **c11sc1**. The lower melting points of succinates may be attributed to an even higher degree of charge delocalisation. The ethylene ($-\text{CH}_2\text{CH}_2-$) group between the two ester functions in the succinates is a flexible saturated hydrocarbon, as opposed to the rigid double bond in the case of maleates. This might well allow both ester functions to be involved in dipolar interactions with the pyridinium ring (Fig. 3) directly with the N^+ centre, but also with the α -carbon atoms as well, thus spreading the charge much more widely. This further reduction in charge density might then reduce the melting point below room temperature. Note that moving from $\text{CH}=\text{CH}$ to CH_2CH_2 generally *increases* melting points, e.g. as seen in the 'hardening' of unsaturated fats by hydrogenation.

3.4. Micellisation behaviour

All surfactants show typical surface activity behaviour and the surface tension/concentration curves exhibit typical

Table 7
Surface activity and thermal data for alkyl pyridinium bromide maleate and succinate diesters

Surfactant	cmc (10^3 mol dm^{-3})	γ_{cmc} (mN m^{-1})	pC ₂₀	$\Gamma_{\text{max}} \times 10^{-6}$ (mol m^{-2})	A (\AA^2)	$\Delta G_{\text{m}}^\circ$ (kJ mol^{-1})	Melting point (°C)	T_k (°C)
CPB	1.37	39.5	3.2	1.1	150	-54	75–77	16
c1mc11	11.1	45.2	1.8	1.2	141	-43	71.5–73	16
c6mc6	8.2	33.7	2.6	1.7	97	-45	42–43.5	24
c10mc2	1.78	41.8	2.9	2.2	74	-53	47–49	34
c12mc2	0.68	41.8	3.3	1.8	92	-58	40–42.5	< 15
c1sc11	22.1	41.8	1.8	1.3	124	-40	oil	< 15
c6sc6	48.2	34.4	2.2	8.7	190	-36	oil	< 15
c10sc2	1.21	27.4	4.1	1.2	140	-55	oil	< 15
c12sc2	0.23	29.5	4.9	9.5	175	-63	55.5–56.5	28

For cmc, γ_{cmc} , pC₂₀, $\Delta G_{\text{m}}^\circ$, see text; Γ_{max} , excess surface concentration; A, area occupied per molecule; T_k , Kraft temperature.

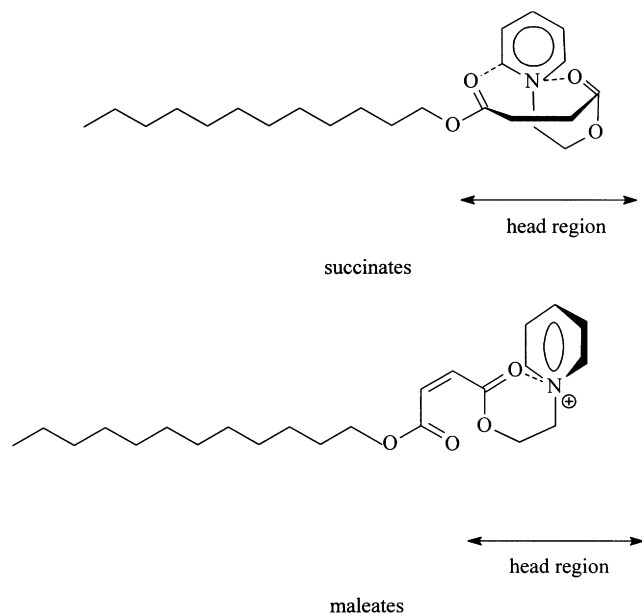


Fig. 3. Possible charge delocalisation structures in maleate and succinate species **c10mc2**, **c12mc2**, **c10sc2** and **c12sc2**.

shapes for surfactants (exemplified in Fig. 4). A summary of the data obtained from these curves is shown in Table 7. Interestingly the variation in the cmc of these molecules is very large considering the only difference is the position of the maleate group along the hydrophobic tail. Tail-type and head-type analogue surfmers have been reported to show distinct cmcs [29]. Cationic azo-surfactants [30] of similar architecture to the surfactants studied in this work (i.e. a head-group, a hydrocarbon chain of variable length, a rigid function (azo) and a hydrophobic tail), also showed variable cmc values; however, the differences are not so pronounced as that exhibited by the amphiphiles in this study. If the **c10mc2** and **c12mc2** surfmers are compared, the longer-chain surfmer **c12mc2** predictably exhibits a somewhat lower cmc than that of **c10mc2**, both being in the range of alkyl pyridinium bromides [31]. This behaviour has been reported previously for similar molecules when the distance between the head group and

the maleate function was kept constant whilst varying the alkyl chain [32,33].

In an attempt to understand the unusual behaviour of the cmc of the surfactants in the maleate series, data available for alkyl pyridinium bromides [31] were used to generate a relationship between the number of methylene units in the hydrophobic tail and the cmc (Table 8 and Fig. 5) [34]. Some authors have used this approach to determine the hydrophobic equivalence of a polymerisable function in terms of number of methylene units [35,36]. However, the application of such a relationship obtained experimentally for one homologous series to a different type of homologous series has proven to be not very accurate [19], but it is useful if it is treated as a qualitative guide. León et al. estimated that the itaconate group ($-\text{O}_2\text{CCH}_2\text{C}(\text{=CH}_2)\text{CO}_2-$) corresponds to about three methylene groups in the hydrophobic tail of a surfactant [37]. Since the vinyl group can be regarded as corresponding to one methylene, the two OCO groups will be equivalent to about one methylene unit. From these values, the estimated value for a maleate function ($-\text{O}_2\text{CCH}=\text{CHCO}_2-$) will be around 2–3. The data in Table 8 shows that significantly different values for the methylene group equivalence are obtained for the maleate compounds studied in this work. The lower cmc surfmers, i.e. **c10mc2** and **c12mc2**, suggest that the maleate unit is equivalent to approximately three methylene units as indeed are the succinate groups in **c10sc2** and **c12sc2**. With these molecules the cmc data is close to the value for **CPB** which has 16 aliphatic C atoms. In contrast the other members of the series, **c1mc11** and **c6mc6**, indicate that the maleate function contributes only about one methylene group to the hydrophobicity. It is clear, therefore, that the surface activity is affected not only by the presence of the maleate function but also by its position. In addition the results confirm the difficulty in using one surface activity/structure relationship to predict the behaviour of another unrelated structural series.

The Gibb's free energy of micellisation can be used as an indication of the tendency of a given surfactant to micellise. In a very simplistic manner, it can be said that the more

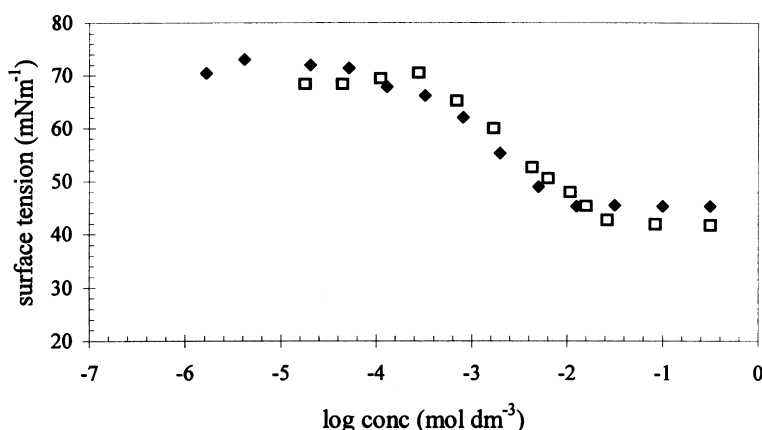


Fig. 4. Typical surface tension/concentration curves for: (□) **c1mc11** and (◆) **c1sc11**.

Table 8
Hydrophobic equivalence of the maleate function in terms of number of aliphatic methylene carbon atoms

Surfmer	No. C atoms deduced from graph ^a	No. actual C atoms in tail	No. C atoms=maleate diester group
c1mc11	12.4	11	1.4
c6mc6	12.9	6 + 6	0.9
c10mc2	15.2	10 + 2	3.2
c12mc2	16.7	12 + 2	2.7

^aSee Fig. 5.

hydrophilic the molecule the less the tendency to micellise, since the hydrophobic effect is less demanding. In the maleate series, for example, surfmer **c1mc11** has the least negative value for ΔG_m , whereas **c12mc2** has the highest negative value, denoting the lower tendency of the former to micellise and the more hydrophobic nature of the latter.

From the comparison of the cmc values of both the maleate and succinate series, the large difference in the cmc of compounds **c1/c11** and **c6/c6** is very obvious, as is the similarity of **c10/c2** and **c12/c2**, again two well-differentiated behaviours. The low cmc compounds (**c10/c2**, **c12/c2**) are those with a well-defined hydrocarbon chain and 'head region'; in other words, their general molecular geometry is close to that of a conventional surfactant, and as such they behave in a similar way, having a cmc in the range of structurally comparable non-polymerisable surfactants [31]. The presence of the maleate double bond does not seem to affect the cmc of these surfactants significantly. As mentioned before, the succinates may well have a lower charge density in the head group than the maleates; nonetheless, in the **c10/c2** and **c12/c2** species, the length of the straight chain seems to be the determining factor in the micellisation behaviour, while the decreased charge density accounts only for the small differences in cmc.

Surprisingly, the **c1/c11** and **c6/c6** pairs of molecules show very different cmcs to those displayed by the other two couples. Moreover, there is a significant difference in cmc between the maleate and succinate analogues, with the succinates having the higher values [31]. The presence of a

polar group in the tail-end of the **c1/c11** species may to some extent 'hydrophilise' the hydrocarbon chain allowing some interaction with water and hence overall making the amphiphile more water-compatible. As a result the tendency for micellisation would be expected to be reduced; whereas in the case of, say, **c10/c2** the tail is a 'fully hydrophobic' hydrocarbon chain. Nevertheless the increase in the cmc by a factor of ~ 10 for the **c1/c11** versus **c12/c2** maleates and by a factor of ~ 20 for the **c1/c11** versus **c12/c2** succinates is remarkable bearing in mind that the only significant change in the structure is the position of the maleate/succinate group.

Rationalising the difference in cmc between the **c1/c11** maleate and succinate (~ 2), and particularly between **c6/c6** maleate and succinate (~ 6) is rather difficult. The high values for the succinates suggest an overall more hydrophilic nature, but on balance $-\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2-$ is probably more hydrophobic than $\text{O}_2\text{CCH}=\text{CHCO}_2-$. Other factors must therefore be considered. One is packing ability within the micelle core. Could the succinate group pack with more difficulty than the maleate, and hence reduce the tendency to micellise? Since the maleate is a more rigid function with therefore fewer conformations available to it, this does not seem very likely. Could the maleate groups give rise to weak polar interactions possibly involving the π electron clouds and ester groups or π electrons in adjacent molecules? This seems a more likely possibility, and a positive interaction of this nature would of course encourage micellisation and reduce the cmc relative to a succinate analogue.

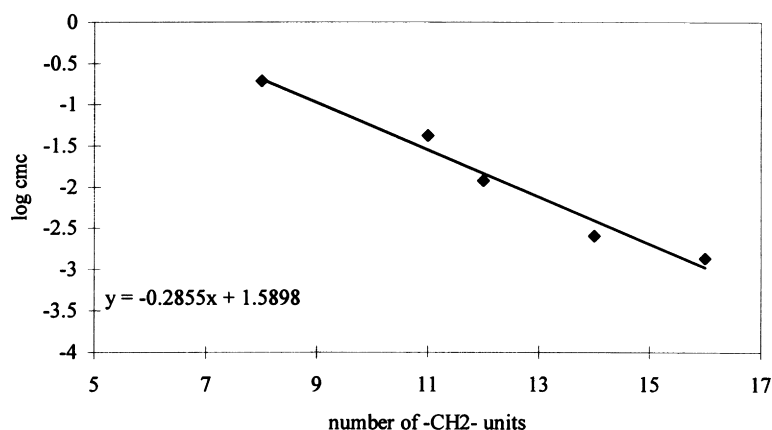


Fig. 5. Relationship between cmc and number of carbon atoms in hydrocarbon chain for alkyl pyridinium bromides.

3.5. Surface activity

The value of the surface tension at the cmc, γ_{cmc} , indicates the extent of interaction between water and surfactant molecules at the interface. The lower the γ_{cmc} value the weaker this interaction and the more hydrocarbon-like is the layer of molecules. Both the **c1/c11** maleate and succinate, have a higher γ_{cmc} than **CPB** indicating more interaction with water and a less hydrophobic surface than in the case with **CPB**. However, the values fall in the range 35–45 mN m⁻¹ typical of cationic surfactants [38]. Interestingly the γ_{cmc} for both **c6/c6** maleate and succinate are both lower than that for **CPB**, indicating less interaction with water and a more hydrophobic surface layer. This seems strange at first, but may reflect some positive intermolecular interaction between maleate–maleate groups and succinate–succinate groups when located in the middle of the hydrocarbon chain.

The data for the **c10/c2** and **c12/c2** maleates and succinates is very interesting. In the case of maleates the γ_{cmc} data are similar to those of the **c1/c11** maleate and succinate and **CPB**, and these surfactants can be regarded as functioning normally. The exact γ_{cmc} values are a little above that for **CPB** suggesting more interaction with water and a less hydrophobic layer than with **CPB** but the difference is small. The very low values for the succinates are more in-keeping with data for nonionic and zwitterionic surfactants [18] than for cationic, and suggest very tight packing at the air–water interface and a very hydrophobic layer. This only seems possible if the ionic headgroups are shielded in some way, and this is totally consistent with the structure proposed earlier (Fig. 3) in which the two carbonyl functions of the succinate interact strongly with the cationic N centre effectively reducing the charge density.

The parameter pC_{20} is the negative logarithm of the concentration that a surfactant needs to decrease the surface tension of water by 20 mN m⁻¹, which is an indication of the tendency for a given amphiphile to adsorb. The values of γ_{cmc} are in good agreement with those of pC_{20} .

The area occupied by the molecules within the maleate series varies considerably with the position of the copolymerisable function (Fig. 6). While **c1mc11** occupies the largest area, as the maleate moiety shifts towards a position closer to the hydrophilic head, the area needed to accommodate the molecule become smaller. This tendency can be rationalised in terms of ‘the looping’ of surfmers [39] when the polymerisable function is at the end of the tail. In isolation the maleate moiety is more polar than the hydrocarbon chain, and therefore tends to want to locate in a more hydrophilic environment at the interface, i.e. in contact with water. Amphiphiles **c10mc2** and **c12mc2** occupy an area comparable to that in the range of other **c10** maleate sulfonates [32] and many other simple ionic surfactants. They all possess a long hydrophobic tail and a hydrophilic head region, and can be regarded as normal ionic surfactants. In contrast, **c6mc6** occupies an area halfway

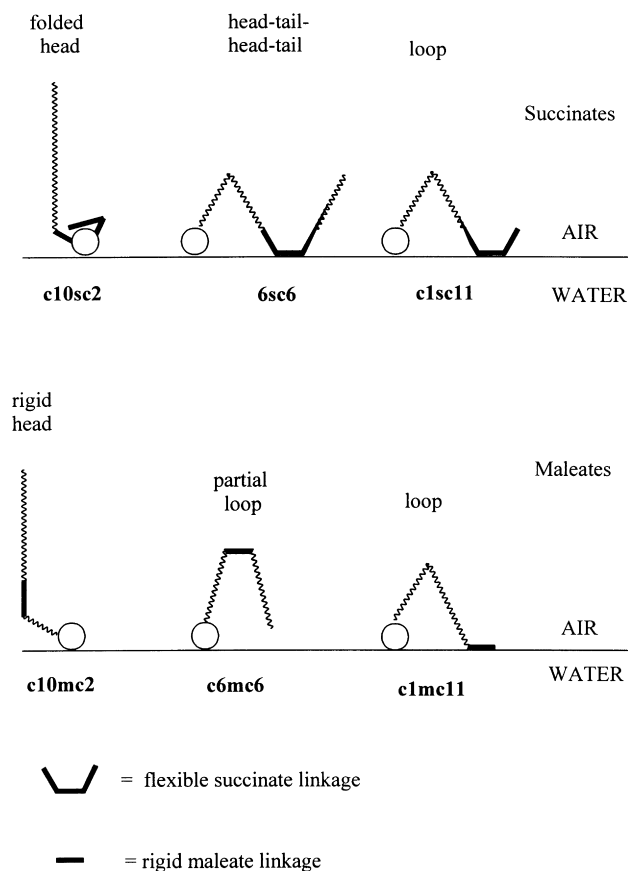


Fig. 6. Possible conformations of the maleate and succinate surfactants at the air–water interface.

between that of **c1mc11** and **c10mc2**. In this case, whilst there is not a full loop involving the maleate function located at the interface, the tail may not be able to adopt a fully perpendicular conformation owing to the rigidity of the *cis* double bond in the maleate, and therefore whilst needing less area than **c1mc11** it requires more area than **c10mc2**.

The succinates in general occupy a larger area than their unsaturated analogues. In the case of the **c10/c2** and **c12/c2** succinates this is reasonable if the two ester groups do indeed interact strongly with the cationic N centre (Fig. 6). The effect anticipated would be to create a larger more diffuse headgroup, occupying more area. The **c1/c11** succinate species behaves like the maleate and occupies a very similar area. Again this suggests that it formed a full loop at the interface. However, in the case of the **c6/c6** pair of molecules, the area occupied by the succinate is almost double that needed by the maleate and indeed is the largest of all the surfactants studied. The more flexible succinate function would in principle permit the molecule, to behave, in effect, as a ‘head-tail–head-tail’ type of amphiphile [40,41] and this conformation at the surface would explain the large area occupied by this molecule. However, the γ_{cmc} of the **c6/c6** succinate is low and very similar to that for the **c6/c6** maleate, and so it is difficult to argue a unique ‘head-tail–head-tail’ conformation on these grounds. All

the data are therefore not totally consistent with a single molecular model and further investigation is needed to clarify the position further.

4. Conclusions

A series of alkyl pyridinium bromide maleate and succinate diester surfactants have been synthesised and their molecular structure characterised. The surface activity behaviour of these novel amphiphiles depends significantly on the position of the maleate or succinate function along the hydrophobic tail of the surfactant. Two well-differentiated groups are observed: those molecules with a long hydrocarbon chain and the maleate or succinate moiety lying close to the hydrophilic head; and those with the maleate or succinate moiety located towards the end of the tail. With the first group, interaction between the maleate or succinate with the pyridinium ring disperses the charge making these molecules behave similarly to a conventional amphiphile with a rather large headgroup. With the second group the maleate or succinate residues tend to disrupt the conformation of the tail and consequently these molecules display enhanced hydrophilic character. They have, for example, cmc values 10-fold larger than might otherwise be expected and appear to adopt a looped conformation at the air–water interface.

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