Novel quaternary ammonium amphiphilic (meth)acrylates: 1. Synthesis, melting and interfacial behaviour*

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A number of novel quaternary ammonium amphiphilic (meth)acrylates have been prepared in good yield. One series has the polymerizable methacryloxy group attached close to the onium ion headgroup, while the other has the polymerizable group attached at the opposite end of the hydrophobic alkyl chain. The melting points, critical micelle concentrations (c.m.c.) and surface-active properties of each have been investigated. The melting points of the first group show a U-shaped minimum as a function of the methylene group content of the hydrophobic chain. The c.m.c. values of these are in general lower than analogous alkyltrimethylammonium bromides of the same chain length, indicating the polymerizable group to be an essential contributor to the hydrophobic micelle core, and probably intramolecularly associated with the onium ion headgroup. The surface tension at the c.m.c. ($\gamma_{c.m.c}$) and the average area occupied by these molecules at the water–gas interface confirm this. The c.m.c. values of the second group suggest that the terminally positioned polymerizable groups do not contribute to the hydrophobic micelle core, and indeed are located at the aqueous interface, with each amphiphile adopting a 'looped' conformation. The $\gamma_{c.m.c}$ and average area per molecule at the water–gas interface also confirm this.

(Keywords: amphiphilic polymerizable monomer; micellization and surface activity)

INTRODUCTION

Amphiphilic species are molecules with both a hydrophobic and a hydrophilic component in their structure. Simple salts of long-chain fatty acids and long-chain alkyl sulphates and alkylbenzene sulphonates are amongst the most important, although nowadays a wide range of anionic, cationic, nonionic and zwitterionic amphiphiles are available[1]. In general these species are molecularly soluble in water at low concentrations, but form micellar aggregates at high concentrations[2]. Furthermore, they are generally surface-active and many form the basis of detergent systems. Amphiphiles with two oligomethylene chains per ionic or polar headgroup are generally insoluble in water, but on sonication will form multilamellar vesicular structures[3]. Recently, there has been considerable interest in polymerizable analogues of vesicle-forming amphiphiles, in order to produce polymerized vesicles with enhanced stability. Such species might be useful in drug encapsulation and release, in solar energy harvesting, in microelectronics, etc.[4] In contrast to this, the synthesis and study of water-soluble polymerizable amphiphiles with a single oligomethylene chain has received considerably less attention. It is monomers of this type, carrying a quaternary ammonium group, that are the subject of this and the following paper.

The term 'polysoap' was certainly in use over 30 years ago[5], when it was used somewhat incorrectly to describe the dodecyl salt of poly(2-vinylpyridine). Since the term 'soap' applies strictly to the salts of long-chain fatty carboxylic acids, a more appropriate name would be polyamphiphile. Polysoap solutions containing a copolymer of styrene and potassium styryl undecanoate were described by Sinha and Medalia[6], and the synthesis of the precursor monomeric vinyl soaps was published a year later[7]. Since then, polymerizable amphiphiles have been studied infrequently (see references in the following paper) although their potential for use in emulsion polymerizations, and in the synthesis of structurally well defined polyamphiphiles, has recently stimulated new interest in those molecules.

We have already reported our preliminary work on some amphiphilic (meth)acrylate-based quaternary ammonium and carboxylate salts, along with two nonionic amphiphilic methacrylate monomers[8]. The recent disclosure by a Japanese group of their work on long-chain alkyl salts of *N*,*N*-dimethylaminoethyl methacrylate[9] (DMAEMA) has prompted us to report our findings with a much wider range of these and related amphiphilic monomers (I–V). This paper deals with synthetic aspects and the properties of the monomers, and the following paper describes the polymerization behaviour.

EXPERIMENT AND RESULTS

Materials

In general these were standard laboratory reagents and were used as supplied. Cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DDAB) were recrystallized from acetone. The water used for determining critical micelle concentrations and for the surface tension studies was doubly distilled, and had a conductivity of ~1 × 10^{-6} mho cm^{-1} at 25°C. The solvents used to generate the surface tension calibration curve were analytical grade.

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* This paper, together with Part 2 of this series, is dedicated to Professor Dr G. Manecke of the Institute of Organic Chemistry, Freie Universität, Berlin

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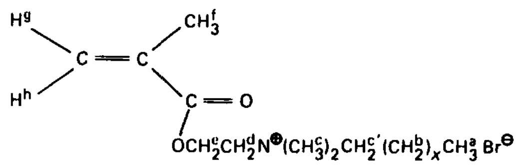
I

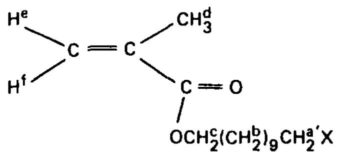


Monomer	Ia,	b,	c,	d,	e,	f,	g,	h,	i,	j,	k,	l
x	1,	2,	3,	4,	5,	6,	7,	8,	10,	12,	14,	16

II $CH_2{=}C(CH_3)CO_2CH_2CH_2N^{\oplus}(CH_3)_2(CH_2)_{10}CH_2OH\ Br^{\ominus}$

III $CH_2{=}C(CH_3)CO_2CH_2CH_2O{\cdot}CO(CH_2)_{10}X$

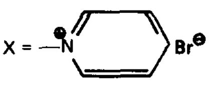
IV



V $CH_2{=}CHCO_2(CH_2)_{11}X$

IIIa, IVa, Va: $X = -N^{\oplus}(CH_3^a)_3\ Br^{\ominus}$

IIIb, IVb, Vb: X =



Analyses

^1H n.m.r. spectra were recorded on a Perkin–Elmer R32, 90 MHz spectrometer; elemental microanalyses were performed on a Carlo Erba Elemental Analyser 1106; and melting points were determined on a Gallenkamp Digital Melting Point Apparatus.

Preparation of quaternary ammonium salts of N,N-dimethylaminoethyl methacrylate (I and II)

These were prepared by direct reaction of DMAEMA with the appropriate 1-bromoalkane or 11-bromoundecan-1-ol in the case of II. Typically DMAEMA (0.166 mol) was mixed with bromoalkane (0.083 mol) without any additional solvent. After the addition of a small portion of hydroquinone to inhibit any spurious radical polymerization, the mixture was stirred overnight at 50°C. The solid product which formed was washed several times with dry ether to remove the excess DMAEMA. Finally, it was recrystallized from acetone and dried under vacuum at room temperature. *Table 1* records the yields of each salt obtained, along with their melting points and elemental microanalyses. ^1H n.m.r. (90 MHz) spectra yielded the following chemical shifts (δ, $CDCl_3$):

H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h
0.9	1.3	3.5	4.2	4.7	1.9	5.6	6.1

($H^a \sim 0.7$ for Ia; $H^a \sim 4.2$ for II; $H^b \sim 1.1$ for Ia; $H^{c'}$ appears as a shoulder on H^c).

The integrated ^1H n.m.r. spectra were satisfactory in all cases, although as a result of some isomeric distribution in the starting 1-bromoalkanes, the integration of H^b did show poorer correlation for the longer chains.

Preparation of quaternary ammonium salts (III, IV and V)

The preparation and characterization of IIIa, b and Va, b have been reported before[8]. Compounds IVa, b were prepared similarly to Va, b, replacing acryloyl chloride with methacryloyl chloride in forming the methacrylate derivative of 11-bromoundecan-1-ol. The results of these preparations are shown in *Table 1*. ^1H n.m.r. spectra (90 Hz), CD_3OD) yielded the following chemical shifts (δ):

	H^a	$H^{a'}$	H^b	H^c	H^d	H^e,H^f
IVa	3.1	3.1	1.3	4.1	1.9	5.8–6.0
IVb	8–9.2*	4.8	1.3	4.1	1.9	5.8–6.0

Determination of critical micelle concentration (c.m.c.) of monomers in water

Critical micelle concentrations were determined from conductivity[10], dye absorption[11] and surface tension

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* Characteristic pattern for pyridinium ion ring protons

Table 1 Synthesis and characterization of monomers Ia–l, II, IVa and IVb

Compound	Yield (%)	Melting point (°C)	Elemental microanalyses							
			Calculated (%)				Found (%)			
			C	H	N	Br	C	H	N	Br
Ia	70	138	47.1	7.9	5.0	28.6	47.0	8.0	5.0	28.4
Ib	85	106	49.0	8.2	4.8	27.2	48.9	8.2	4.9	27.2
Ic	83	92	50.7	8.4	4.6	26.0	50.5	8.4	4.6	26.0
Id	62	89	52.2	8.7	4.4	24.8	51.8	8.5	4.3	24.8
Ie	99	86	53.6	8.9	4.2	23.8	53.3	8.8	3.7	22.9
If	64	84	54.9	9.1	4.0	22.9	54.6	9.1	4.0	22.9
Ig	88	83	56.0	9.3	3.9	22.0	55.5	9.1	3.6	21.8
Ih	69	77	57.1	9.5	3.7	21.2	57.0	9.2	3.4	21.6
Ii	90	77	59.1	9.9	3.5	19.7	58.6	9.9	3.5	19.7
Ij	91	105	60.8	10.1	3.2	18.4	60.3	10.4	3.1	18.7
Ik	88	131	62.3	10.4	3.0	17.3	62.7	10.8	3.0	17.6
Il	89	168	63.6	10.6	2.8	16.3	63.1	10.6	2.6	16.6
II	85	129	55.9	9.3	3.4	19.6	55.2	9.4	3.2	20.3
IVa	84	158	57.1	9.5	3.7	21.2	56.3	9.4	3.9	21.5
IVb	86	46	60.3	8.0	3.5	20.1	59.2	8.0	3.4	21.2

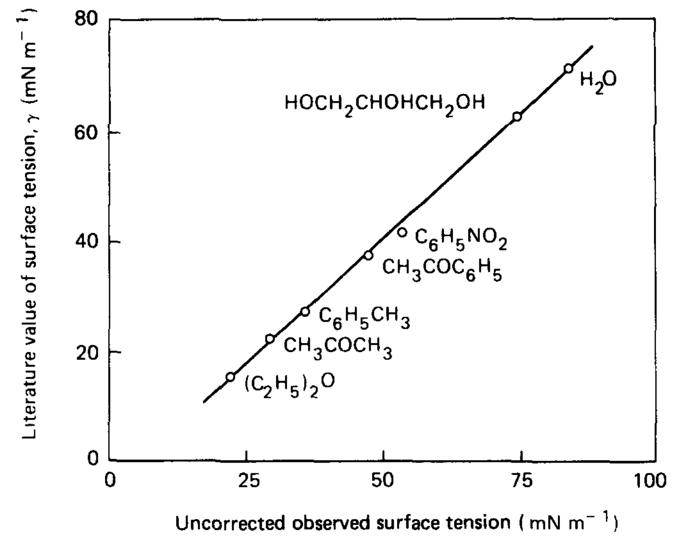

Figure 1 Surface tension calibration curve

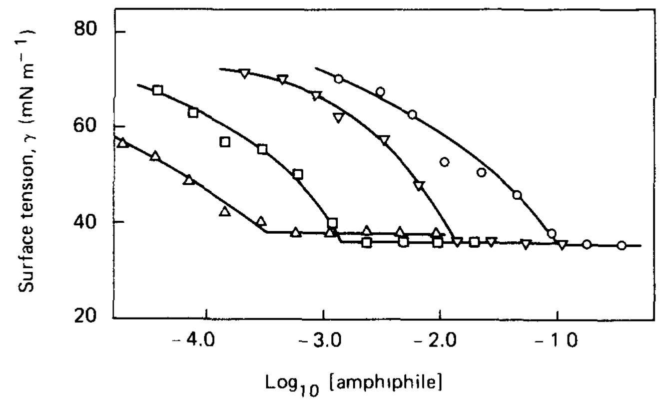

Figure 2 Typical plots of surface tension γ *versus* log(concentration): ○, Ie; ▽, Ih; □, Ij; △, Il

measurements. Details of our use of the first two methods have already been reported[8], and included there are typical examples of the appropriate plots from which c.m.c. values were deduced.

Surface tension method

The equilibrium surface tension of an aqueous solution of a surface-active agent decreases steadily as the bulk concentration of the agent is increased and forces more molecules to become packed into the liquid–gas interface. However, as the c.m.c. is reached and micelles form within the liquid phase, addition of more surfactant simply increases the number of micelles present, and the surface tension becomes essentially constant. Hence the c.m.c. can be determined from the point of inflection of plots of equilibrium surface tension *versus* log(concentration)[12–14]. The particular advantage of this method is that the accuracy is nearly the same for both long- and shorter-chain amphiphiles because the value of the surface tension changes over more or less the same magnitude[15].

Equilibrium surface tensions were measured using the Du Nouy platinum ring method[16] employing equipment supplied by Cambridge Instrument Co. Ltd. Although, in principle, this is an absolute method, in this work it was found to be more convenient to calibrate the instrument using pure solvents of known surface tension at 25°C[17]. The calibration curve is shown in *Figure 1*. In these measurements all glassware was cleaned by immersion for 15 min in a hot solution of saturated potassium dichromate (10 ml) in concentrated sulphuric acid (990 ml), followed by thorough rinsing with conductivity water. In addition, the platinum ring was flamed after being used with each solution.

Typically, a stock solution ($\sim 10^{-1}$–10^{-2} M) of an amphiphilic monomer was prepared in doubly distilled water, and by successive dilution, a series of solutions of decreasing concentration was obtained. Working from the lowest concentration, the surface tension of each solution was measured (utilizing the calibration curve) at 25°C, and a plot of surface tension *versus* log(concentration) was constructed. Typical plots are shown in *Figure 2*, while *Table 2* shows a summary of all the c.m.c. data obtained from the three methods.

DISCUSSION

Syntheses and melting properties of amphiphilic monomers

In devising synthetic strategies for ionic amphiphiles, by the very nature of the latter, it is always better to generate the ionic structure itself in the last synthetic step. This then minimizes the need for the manipulations of intermediate products which are also surface-active, and therefore likely to give rise to isolation and purification problems. When the desired amphiphile is simultaneously a sensitive polymerizable monomer, it is further desirable to introduce the polymerizable group at as late a stage as possible, to avoid problems of spurious polymerization.

In the case of monomers I and II, a single reaction attaches the polymerizable group to the organic framework and simultaneously generates the ionic headgroup. This is, of course, most convenient and the yields and purity (from ^1H n.m.r. spectra and elemental

Table 2 Critical micelle concentrations derived from conductivity, surface tension and dye absorption data[a]

	Critical micelle concentrations × 10² (M)		
Compound	Conductivity	Surface tension	Dye absorption
Ia	no transition detected		
Ib			
Ic			
Id			
Ie	18.0	10.5	4.4
If	4.8	2.9	1.6
Ig	2.4	2.1	0.84
Ih	1.3	1.5	0.66
Ii	0.36	0.25	0.19
Ij	0.11	0.15	0.05
Ik	0.09	0.10	0.05
Il	0.06	0.03	0.03
II	2.5	1.5	1.3
IIIa[b]	4.8	1.6	0.30
IIIb[b]	6.8	3.5	0.21
IVa	1.6	1.0	0.39
IVb[b]	2.1	1.5	0.53
Va[b]	1.4	1.3	1.0
Vb	1.2	1.3	1.0
CTAB	0.09[b]	0.07	0.005[b]
DDAB	4.9[b]	2.3	0.4[b]

[a] At 25°C
[b] Data from ref. 8

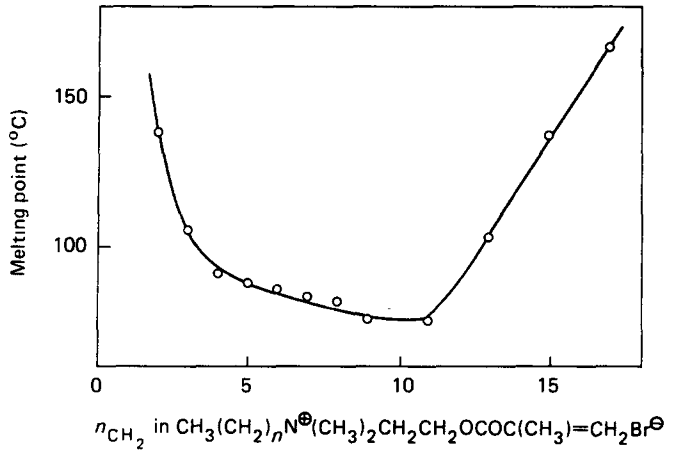

Figure 3 Plot of melting point *versus* alkyl chain length n_{CH_2} in monomers I

microanalyses) of these compounds were most satisfactory (*Table 1*). With monomers III–V, it was first necessary to attach the polymerizable group to the organic framework, then to generate the ionic headgroup. Nevertheless, these two-step processes were also very convenient, and the yields and purity of the products quite satisfactory (*Table 1* and ref. 8).

Monomers Ia–l represent a homologous series, and the melting points of these solids are plotted in *Figure 3* as a function of the number of methylene groups within the R– substituent in $CH_2=C(CH_3)CO{\cdot}OCH_2CH_2N^{\oplus}$-$(CH_3)_2RBr^{\ominus}$. This shows a remarkable U-shaped dependence. In general, it has so far proved impossible to predict the melting point behaviour of amphiphilic species with any certainty, and many apparent anomalies remain. It is well known, however, that traces of residual water can cause large shifts in apparent melting points, and indeed water plays a significant role in determining the phase behaviour of soaps and synthetic detergents[18]. Monomers Ik and Il did show some evidence under the optical microscope of an additional phase change around 90 and 100°C, respectively, and indeed in our hands cetyltrimethylammonium bromide, m.p.(decomp.) > 200°C, showed a similar change at ~85°C. Dodecylpyridinium bromide also behaves in this way, and in this case the temperature of the secondary phase change does vary with moisture content[19]. Despite a number of attempts to crystallize and dry these monomers to a more anhydrous state, no increase in the observed melting point could be achieved. It appears, therefore, that the melting points in *Figure 3* are intrinsic, and that the U-shaped dependence on the methylene group content is real. A tentative precedent for such a minimum in the melting point behaviour is afforded by ammonium and alkali-metal salts of fatty acids[20]. Furthermore, such behaviour can be rationalized in molecular terms. When the substituent R– is a short chain, the monomers are highly salt-like and display high melting points. As the chain length of R– increases, and hence the organic nature of the molecule rises, the melting point falls. However, as the chain length increases further the melting point rises again in the same way as the melting point of long-chain paraffins.

In the case of the monomers IIa and IVa and IIIb and IVb a consistent relationship emerges between their melting points. That of each pyridinium salt is very much lower than that of the corresponding salt with a trimethylammonium headgroup (*Table 3*). A similar differential exists with the corresponding simple dodecyl salts[19]. This difference probably reflects the higher charge density of the trimethylammonium headgroup, along with its greater symmetry. Both of these factors would encourage tighter packing in the crystal lattice.

Micellar behaviour of amphiphilic monomers

Critical micelle concentrations (c.m.c.) for the monomeric amphiphiles were determined at 25°C by three separate techniques and the results are summarized in *Table 2*. For compounds Ia–d no micellar transition was detected, while the remainder all displayed physical behaviour consistent with a micellization process in water. The homologous series Ie–l showed a progressive fall in the c.m.c. in accordance with the increasing hydrophobic nature of the long-chain alkyl group. The value of each c.m.c. determined from surface tension data corresponded closely with the values obtained from conductivity measurements, which in the case of Ik and Ij agreed well with the values reported by Nagai *et al.*[9] However, in all cases the c.m.c. data from the dye absorption experiments was consistently lower by a factor of 3–10. This pattern has been reported before in the case of both conductivity[21] and surface tension[22] derived data, and most probably results from a disturbance of the micelle structure by the presence of the solubilizate in the case of the dye absorption experiments. Bearing this in mind, the agreement in the data derived from conductivity and dye solubilization experiments on Ik, Ij and Il reported by Nagai *et al.* seems a little strange[9].

For a homologous series of amphiphilic molecules, the c.m.c. values usually obey the empirical relationship:

$$\log(\text{c.m.c.}) = A - Bn_{CH_2}$$

where A and B are constants, and n_{CH_2} is the number of methylene groups in the hydrophobic tail of the amphiphile[23]. Indeed, this relationship also has a sound theoretical basis[24]. In the case of the monomers Ie–l the log(c.m.c.) vs. n_{CH_2} plot is a shallow curve as shown in *Figure 4* (c.m.c. values derived from conductivity data). In particular, at high values of n_{CH_2} the c.m.c. does not change as much as the corresponding c.m.c. for alkyltrimethylammonium bromides (ATMAB) (also shown in *Figure 4*, data derived from conductivity measurements, refs. 25–27). A similar plot (not shown here) using c.m.c. values derived from surface tension data is also curved, though a little more shallow. Both sets of data suggest, therefore, that the net hydrophobic contribution from successive CH_2 groups in the

Table 3 Melting points of polymerizable amphiphiles with trimethylammonium and pyridinium headgroups

	Melting point (°C)	
Compound	$-^{\oplus}N(CH_3)_3$ headgroup	Pyridinium headgroup
III	140	low
IV	158	46
V	130	54
$C_{12}H_{25}-$	>200	125[a]

[a] See ref. 9

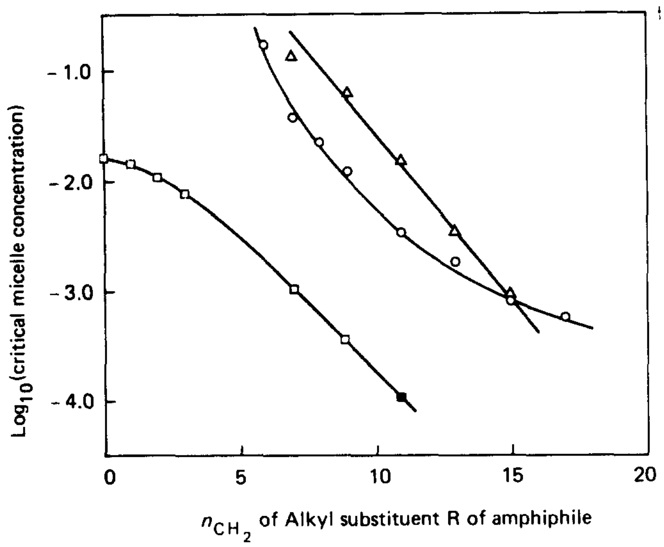

Figure 4 Plots of log(critical micelle concentration) *versus* chain length n_{CH_2} of alkyl substituent R in:
△, $RN^{\oplus}CH_3)_3Br^{\ominus}$ (refs 25–27);
○, $RN^{\oplus}(CH_3)_2CH_2CH_2OCO{\cdot}C(CH_3)=CH_2Br^{\ominus}$;
□, $RN^{\oplus}(CH_3)_2C_{12}H_{25}Br^{\ominus}$ (refs. 25, 29–31);
■, estimated from value for $Cl^{\ominus}$ salt

amphiphile tail is not linear, particularly for higher n_{CH_2} values, in contrast with the ATMAB salts. The presence of the polymerizable group, $CH_2{=}C(CH_3)CO{\cdot}OCH_2CH_2$–, seems to play a significant role.

Comparing, first, the monomers Ie–l with the analogous ATMAB salts, it is clear that the former continue to micellize down to only six CH_2 groups in the main alkyl chain. Furthermore, for values of n_{CH_2} up to 13, c.m.c. values for I are significantly lower than those of each ATMAB salt of the same alkyl chain length. For a typical surfactant chain of $C_{12}H_{25}$– the effect of the $CH_2{=}C(CH_3)CO{\cdot}OCH_2CH_2$– group is equivalent to replacing this group with a CH_3– group in the ionic head, and simultaneously increasing the main alkyl chain to $C_{14}H_{29}$–. This implies that for Ie–j the polymerizable group is associated with the core of the micelle, and makes a significant contribution to the hydrophobicity of the core. For this to be possible, the polarity of the ester substituent must be reduced below its normal level, and also the interaction of the ester with the aqueous interface must be inhibited. Intramolecular interaction between the ester carbonyl group and the onium nitrogen atom via the six-sided structure shown in *Figure 5* would achieve both of these requirements. Furthermore, this would result in a reduction of the charge density of the headgroup, again favouring micellization at lower concentrations. It would also produce a rather more rigid and compact structure for the headgroup than might at first be imagined, and indeed this seems to be the case in practice (see following section on 'Surface activity'). Independent evidence for such an intramolecular interaction is afforded by the facile alkaline hydrolysis of these quaternary nitrogen-substituted esters. Anchimeric assistance via the structure shown in *Figure 5* (see following paper) would indeed be expected to activate these molecules with respect to hydrolysis.

The c.m.c. value for monomer Ik is essentially the same as that of CTAB, and beyond $C_{16}H_{33}$– there is every indication that the relative hydrophobicities of I and each ATMAB salt are reversed. It is known that for chain lengths greater than 16 carbon atoms the correlation between log(c.m.c.) and n_{CH_2} starts to break down, possibly due to excessive coiling or folding of these longer chains[28]. In the case of Ik and Il this folding may well disrupt the relatively rigid cyclic structure of the headgroup, raise the effective charge on the latter and indeed make the methacryloxy substituent available for interaction with water molecules at the interface. In this respect their behaviour starts to parallel that of amphiphiles III and IV (see later), and their effective hydrophobicities fall off rather suddenly.

In order to make a comparison between amphiphiles with an alkyl chain of a fixed length (e.g. $C_{12}H_{25}$–), the c.m.c. data for alkyldodecyldimethylammonium bromides, $CH_3(CH_2)_{11}N^{\oplus}(CH_3)_2RBr^{\ominus}$ (ADDAB), are useful. The conductivity derived c.m.c. data for appropriate examples[25,29–31] are also plotted in *Figure 4*. These show clearly that the behaviour of the dodecyl-substituted monomer, Ii ($n_{CH_2}=11$), corresponds to that of n-hexyldodecyldimethylammonium bromide ($n_{CH_2}=5$), i.e. superficially the $CH_2{=}C(CH_3)CO{\cdot}OCH_2CH_2$– group is analogous to $CH_3(CH_2)_5$– in these dialkyl-substituted dimethylammonium bromides. This confirms that the polar nature of the former group is reduced significantly, and is consistent with the proposed intramolecular interaction with the onium nitrogen atom (*Figure 5*). Nagai *et al.*[9] have also pointed out the similarity in the behaviour of Ii with dodecylbenzyldimethylammonium bromide, implying a similar equivalence of the polymerizable group in Ii with the seven-carbon-atom benzyl group. Recently, the ester grouping –$CO{\cdot}OCH_2CH_2$– has been shown to be equivalent to 1.27 CH_2 groups[32], in the case of a series of bisquaternary ammonium salts. While this observation appears to contradict the results presented here, it is perhaps best regarded as a warning not to take these hydrophobic correlations too far and, in particular, to exercise caution when cross-correlating homologous series of molecules with very different structural characteristics.

Monomer II differs significantly from I because of the presence of the terminal hydroxyl group on the alkyl chain. From *Figure 4* it is possible to predict a c.m.c. value derived from conductivity data of $\sim 7.5\times10^{-3}$ M for monomer II without its terminal hydrophilic group. Thus the presence of the hydroxyl group reduces the overall hydrophobicity of the molecule such that the c.m.c. increases by a factor of ~ 3 to 2.5×10^{-2} M. It is also likely that II adopts a conformation in the micelle such that its hydroxyl group, as well as its ionic headgroup, is located at the aqueous interface (see following section on 'Surface activity').

With regard to the monomers III–V, these all display a

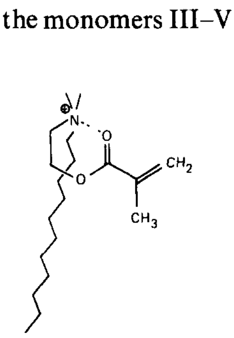

Figure 5 Conformation of monomers Ie–j at micelle–water and water–gas interfaces, showing intramolecular interaction of methacryloxy ethyl substituent with quaternary nitrogen centre

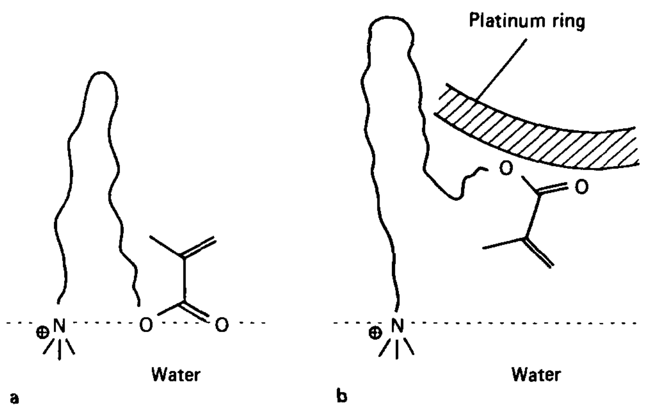

Figure 6 (a) Conformation of monomers III–V at micelle–water and water–gas interfaces showing 'loop' or 'wicket-like' formation. (b) 'Bridging' action of monomers III–V as platinum ring moves through water–gas interface

micellar transition and the c.m.c. values fall in the narrow range $(1.2–6.8) \times 10^{-2}$ M for conductivity derived values, and $(1.3–3.5) \times 10^{-2}$ M for corresponding surface-tension derived values (*Table 2*). As before, data from the dye absorption measurements are lower, and relate less realistically to the unperturbed micellar structure. These molecules are structurally quite different from the monomers I, since the polymerizable and ionic groups are situated at opposite ends of the long hydrophobic chain. Comparison of the conductivity derived c.m.c. values with the data for alkyltrimethylammonium bromides in *Figure 4* suggests that III behaves similarly to decyltrimethylammonium bromide, and IV and V similarly to the dodecyl salt. In other words, in these amphiphiles the groups $CH_2{=}C(CH_3)CO{\cdot}OCH_2CH_2O{\cdot}CO–$, $CH_2{=}C(CH_3)CO{\cdot}O$ and $CH_2{=}CHCO{\cdot}O$ appear to make no contribution to the overall hydrophobicity of the molecules. This, of course, is in complete contrast to the situation with the amphiphiles I. One possible reason for this is that, like monomer II, the terminal location of the (meth)acryloxy group allows each of these amphiphiles to adopt a loop-like conformation, such that the dipolar terminal group can optimize a weak interaction with water molecules at the aqueous–organic interface (*Figure 6a*). Again, this contrasts sharply with the picture presented earlier for I (*Figure 5*), but is consistent with the surface activity behaviour of the two groups of amphiphiles (see following section on 'Surface activity').

Comparison of the data for IIIa–Va with IIIb–Vb in *Table 2* suggests, perhaps surprisingly, that a change from the $-^{\oplus}N(CH_3)_3$ to the pyridinium ion headgroup does not produce a significant change in the micellization behaviour for a given long-chain structure. This confirms data already available in the literature[19,25].

Surface activity of amphiphilic monomers

All of the amphiphilic monomers reduced the water–gas equilibrium surface tension γ of solutions in a classic manner, and *Figure 2* shows representative examples of the $\gamma/\log_{10}C$ plots from which the c.m.c. values in *Table 2* are derived. *Table 4* shows the values of γ at the c.m.c., $\gamma_{\text{c.m.c.}}$, for each amphiphile. Two groups can be distinguished. Molecules Ie–l display $\gamma_{\text{c.m.c.}}$ below $\sim 40\,\text{mN m}^{-1}$ and behave similarly to DDAB and CTAB. Molecules II–V display $\gamma_{\text{c.m.c.}}$ values consistently higher, up to $\sim 46\,\text{mN m}^{-1}$. The intrusion of amphiphilic molecules into the surface layer and the replacement, in effect, of some water molecules by hydrocarbon is generally regarded as the source of the reduction in surface tension. The intermolecular attraction between water molecules and nonpolar hydrocarbon segments is of course much less than that between water molecules themselves, and the contracting power of the surface, and hence the surface tension, is reduced. With II–V the terminal hydroxyl and polar (methy)acryloxy ester groups respectively are also likely to be involved at the surface (*Figure 6a*), as previously argued. It would be expected that such groups would interact somewhat more strongly with water molecules than do simple hydrocarbons and, therefore, retain a little more of the original contracting power. This would then explain the consistently higher $\gamma_{\text{c.m.c.}}$ values for these amphiphiles. In the case of Ie–j the methacryloxy substituent is less available for interaction with water, again as argued earlier, and hence the $\gamma_{\text{c.m.c.}}$ values for these correspond more closely to that for CTAB and DDAB. Earlier evidence suggests that the methacryloxy group in Ik and Il is, however, more available, and while the values for these are indeed a little higher than those for Ie–j, they are no higher than those for CTAB and DDAB. In considering these molecular interactions it is important to bear in mind the macroscopic experiment from which these molecular parameters are deduced. When the platinum ring enters and is pulled through the water–gas interface, there exists the possibility that polar groups weakly bound at the interface may in fact interact with the platinum metal surface. Amphiphiles II–V are particularly suitable to allow such an interaction, maintaining their ionic group firmly in the lower interface, while allowing the more weakly interacting terminal –OH or ester group to bind to the platinum metal surface (*Figure 6b*). In contrast all the amphiphiles Ie–l, including Ik and Il, cannot behave in this way, since the methacryloxy group is bound closely to the ionic headgroup (*Figure 5*). The 'bridging' action of II–V (*Figure 6b*) may, therefore, make a major contribution in raising the apparent $\gamma_{\text{c.m.c.}}$ value. Nonintrusive techniques for estimating $\gamma_{\text{c.m.c.}}$ would not, therefore, be expected to

Table 4 Water–gas surface properties of polymerizable amphiphiles Ia–l, II, III, b, IVa, b and Va, b[a]

Amphiphile	$\gamma_{\text{c.m.c.}}$ (mN m^{-1})	$\text{d}\gamma/\text{d}\log C$ $\times 10^3$	A (Å^2)
Ie	35.7	23.8	80
If	37.5	21.7	87
Ig	34.8	27.0	70
Ih	36.2	37.0	51
Ii	35.0	33.0	57
Ij	36.2	29.4	64
Ik	39.0	13.0	146
Il	38.0	16.1	118
DDAB	40.0	31.3	61
CTAB	37.5	31.3	61
II	43.3	18.9	100
IIIa	42.2	16.1	118
IIIb	45.7	12.1	157
IVa	43.0	16.7	113
IVb	38.1	18.2	104
Va	41.3	20.0	95
Vb	42.5	10.9	174

[a] At 25°C

produce this difference. Likewise metals with higher reactivity than platinum would be expected to maximize the effect, as indeed would terminal polar groups with a stronger coordinating power.

Using the Gibb's adsorption isotherm for a 1:1 ionic amphiphile in the absence of electrolyte, it is possible to calculate the concentration of surface saturation $\Gamma_{\max}$ ($\mathrm{mol\,m^{-2}}$) at the water–gas interface from the linear part of the $\gamma/\log_{10}C$ plots:

$$\Gamma_{\max} = -\frac{1}{2\times 2.303RT}\left(\frac{d\gamma}{d\log C}\right)_T$$

where R is the gas constant, T the absolute temperature, and $(d\gamma/d\log C)_T$ is the slope of the plot at the c.m.c. Furthermore, the average surface area of a molecule in the water–gas interface, A (Å^2), at the c.m.c. is given by:

$$A = 10^{20}/\Gamma_{\max} N_A$$

where N_A = Avogadro's number. The validity of the above form of the Gibbs adsorption isotherm, which includes the factor 2, is still a matter of debate[33]. In view of this, the derived values for A shown in *Table 4* will be regarded simply as an area parameter, whose absolute significance remains to be decided. Of more importance here, however, are the *relative* magnitudes of A. The values for DDAB and CTAB are the same, and consistent with those reported by other workers[34,35]. (Note that molecular models predict an area of 30 Å^2 for alkyl chains aligned perpendicular to the interface[34].) Amphiphiles Ie–j yield A values similar to the alkyltrimethylammonium bromides, and in agreement with the conformationally rigid and compact model proposed for the headgroup of these (*Figure 5*). Molecules II–V, however, yield significantly higher A values, and again this is consistent with the 'loop-like' conformation proposed earlier (*Figure 6a*), in which both ends of the amphiphile are located at the interface. This situation parallels exactly the 'wicket-like' conformation proposed by Menger and Wrenn[34] in the case of quaternary ammonium bola-amphiphiles. (Note that the proportion of molecules II–V in the interface which become detached in interaction with the platinum metal ring in measuring γ as proposed above would be too small to influence this averaged calculation.) Molecules Ik and Il also show high A values, in keeping with the earlier argument that these, and only these, homologues of I have their methacryloxy substituents released from the relatively rigid and compact conformation for independent interaction at the interface.

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