

Novel polymerizable mono- and divalent quaternary ammonium cationic surfactants: 2. Surface active properties and use in emulsion polymerization

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Eight polymerizable monoquaternary ammonium bromide cationic surfactants, and five non-polymerizable analogues have been prepared along with six structurally related polymerizable diquaternary ammonium dibromide cationic surfactants and five non-polymerizable analogues of these. The surface activity properties of all the surfactants have been characterized using surface tension and electrical conductivity measurements. The derived data (critical micelle concentrations, area per molecule at the air/water interface, etc.) have been compared and discussed in terms of the molecular structure of the surfactants and the valency of the salts. All of the surfactants have been employed (singly) as the emulsifier in small scale emulsion polymerizations of styrene and methylmethacrylate. In all cases well defined stable polymer latexes were obtained. The stability of these has also been further probed by the addition of various mono-, di- and trivalent electrolytes. Each emulsion has also been subjected to a freeze–thaw cycle. The stability results are discussed in terms of the molecular structure of the surfactants and, in particular, the efficiency of polymerizable vs non-polymerizable species have been compared and, likewise, the effectiveness of dicationic species vs monocationic ones. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polymerizable divalent quaternary ammonium surfactants; ‘Surfmers’)

INTRODUCTION

Over the last 20 years or so, interest in polymerizable single chain surfactants has accelerated^{1–18}. Typical polymerizable groups which have been exploited are allyl¹⁰, acrylate and methacrylate^{3,7,14}, styryl^{12,18} and acrylamido^{1,4,5}. The polymerizable group is usually part of the main hydrophobic chain, however, at least one research group has polymerized the counterion in the form of a methacrylate ion⁹. The polymerizations which have been studied use thermal and u.v. initiators, and when necessary, gamma radiation. Recently some attempts have been made to review the area^{17,19,20}.

Interest has developed because of the possibility of linking surfactants chemically to a dispersed phase to improve properties²¹. Chemical fixation of surfactants within say a coating formulation might help to prevent unwanted surface adsorption²². Use of polymerizable surfactants in emulsion polymerization where the surfactant can copolymerize with the monomer may enhance the emulsion stabilizing effects over conventional surfactants^{20,23–25} and inhibit subsequent surfactant migration. Polymerization of surfactants onto the surface of alumina or silica and other solids can lead to increased stability of dispersions of these solids²⁶. Also, it

was realized many years ago that polymerization of surfactants can lead to well-defined polymeric surfactants²⁷ and potentially to polymerized micelles^{28,29}.

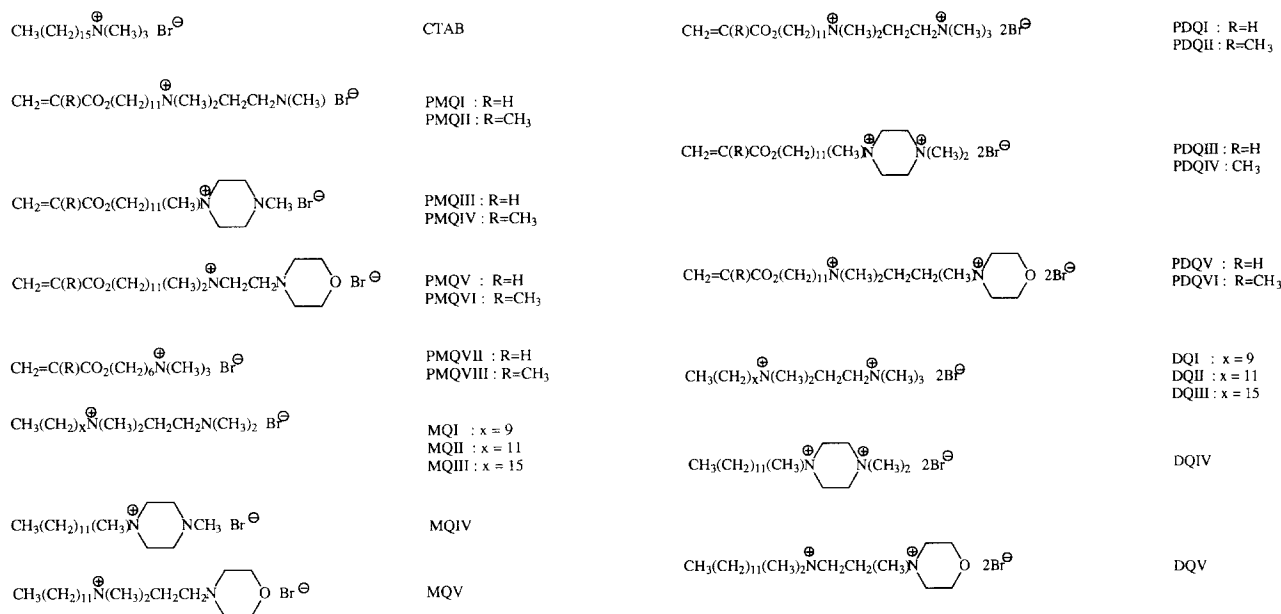
As far as we are aware, to date the exploitation of polymerizable single chain surfactants has focused on structures involving singly charged ionic species or non-ionic systems involving an oligo(oxyethylene) head-group. We have recently reported on the synthesis, structural characterization and homopolymerization of a group of polymerizable divalent quaternary ammonium cationic surfactants³⁰. The present paper quantifies the surface activity behaviour of these molecules and compares this with data on some structurally closely related mono-valent cationic surfactants. It also describes their use in emulsion polymerization. The increased local charge density offered by the dicationic headgroups was thought to offer the potential of improved performance.

EXPERIMENTAL AND RESULTS

Materials

Cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DDTAB) (B.D.H.) were recrystallized from acetone. Surfactants PMQI-VIII and MQI-V (*Scheme 1*) and PDQI-VI and DQI-V

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Scheme 1 Monovalent quaternary ammonium surfactants

Scheme 2 Divalent quaternary ammonium surfactants

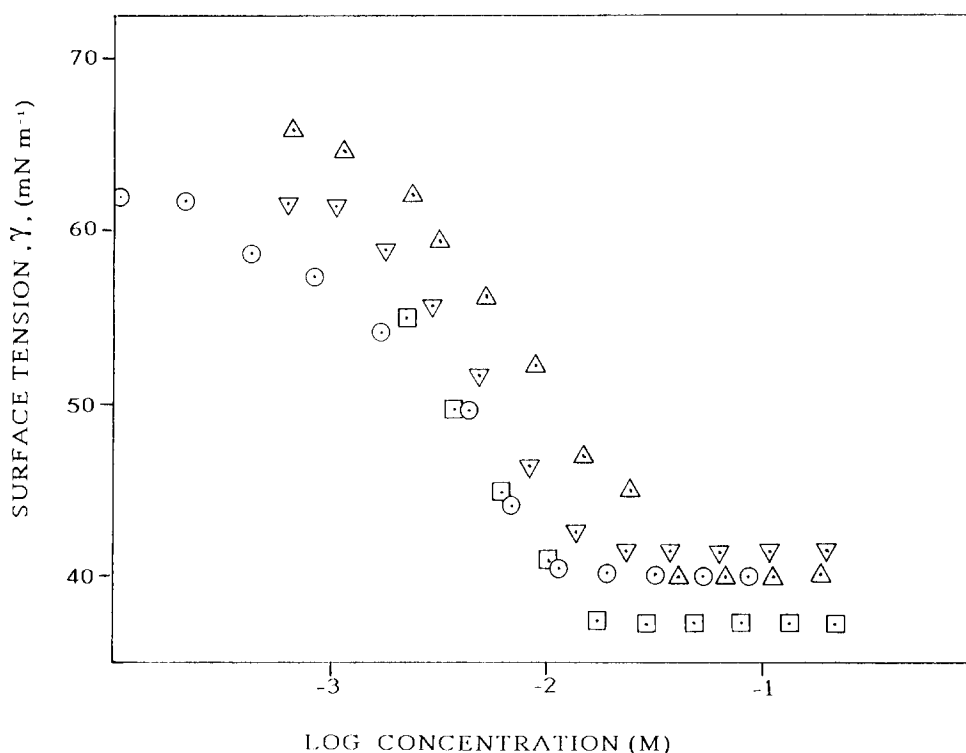


Figure 1 Surface tension, γ , vs log concentration plots for: \circ , PMQ-VI at neutral pH; Δ , PMQ-VI at pH 2.2; \square , PMQ-VI in 1.88 M aqueous ethanol; ∇ , PDQ-VI

(Scheme 2) were synthesized, purified and structurally characterized as reported in Part 1 of this work³⁰. The same designation has been employed here to allow direct correlation. Ethanol was used as supplied (J. Burroughs Ltd) as was azobisisobutyronitrile (AIBN) (Aldrich Chem. Co.). Methyl methacrylate (Aldrich Chem. Co.) was washed with sodium hydroxide (2 M) and water before drying over sodium sulfate. Styrene (Aldrich Chem. Co.) was used as received. Calcium chloride, sodium chloride and trisodium orthophosphate (B.D.H.) and aluminium chloride hexahydrate, and sodium sulfate (Aldrich Chem. Co.) were all used as supplied.

Determination of critical micelle concentration (cmc) of surfactants

Surface tension method. Equilibrium surface tensions (γ) of surfactant solutions were measured at 25°C using the Du Nuoy ring method³¹ employing a tensiometer supplied by White Electrical Instruments Co. Ltd. As in earlier work⁷ we chose to calibrate the instrument using pure solvents of known surface tension³², and the details of our technique have been published⁷. Cmc values were taken at the point of inflection of γ vs log (concentration) plots in the normal way. Typical results for PMQ-VI in water at neutral pH, at pH 2.2 and with

Table 1 Surface activity data^a for polymerizable and non-polymerizable monoquaternary ammonium cationic surfactants in water at 20°C^b

Surfactant	Critical micelle concentration × 10 ² (M)		γ_{cmc} (mN m ⁻¹)	pC ₂₀	$\Gamma_{max} \times 10^6$ (mol m ⁻²)	A_c (Å ²)	ΔG_m° (kJ mol ⁻¹)
	Surface tension	Conductivity					
CTAB	0.09	0.10	37.5	–	1.75	95	–54.6
DDTAB	1.55	1.41	36.5	–	2.13	73	–40.6
PMQ-I	1.04	2.49	38.6	2.72	1.57	105	–42.5
PMQ-II	0.776	2.00	39.3	3.00	1.26	132	–44.2
PMQ-III	0.447	2.30	38.5	3.19	1.45	115	–46.7
PMQ-IV	0.446	2.16	35.5	3.23	1.60	104	–46.7
PMQ-V	1.15	1.40	39.8	2.65	1.51	110	–42.0
PMQ-VI	1.07	2.93	39.8	2.63	1.54	108	–42.3
PMQ-VII } PMQ-VIII }			No transition detected				
MQ-I	3.31	–	37.0	2.12	2.23	75	–36.8
MQ-II	2.51	1.82	35.6	2.57	1.48	113	–38.0
MQ-III	0.105	0.11	39.5	3.71	1.52	109	–53.9
MQ-IV	0.794	2.00	34.0	3.23	1.38	121	–43.9
MQ-V	1.48	1.80	37.2	2.52	1.94	86	–40.8

^a See text for interpretation of symbols

^b Neutral pH

Table 2 Surface activity data^a for polymerizable and monoquaternary ammonium cationic surfactants in water at 25°C at pH = 2.2

Surfactant	Critical micelle concentration × 10 ² (M)	γ_{cmc} (mN m ⁻¹)	pC ₂₀	$\Gamma_{max} \times 10^6$ (mol m ⁻²)	A_c (Å ²)	ΔG_m° (kJ mol ⁻¹)
PMQ-I	1.17	40.0	2.73	1.54	108	–40.1
PMQ-II	2.04	37.6	2.59	0.94	177	–39.2
PMQ-III	2.75	37.6	2.47	0.92	180	–37.7
PMQ-IV	1.24	37.4	2.73	1.03	162	–41.2
PMQ-V	6.46	39.2	2.80	1.24	134	–33.5
PMQ-VI	4.17	39.8	2.08	1.03	162	–35.6

^a Derived from surface tension data, see text for interpretation of symbols

Table 3 Surface activity data^a for polymerizable and non-polymerizable monoquaternary ammonium cationic surfactants in water at 25°C with ethanol as an additive

Surfactant	Critical micelle concentration × 10 ² (M)		γ_{cmc} (mN m ⁻¹)	pC ₂₀	$\Gamma_{max} \times 10^6$ (mol m ⁻²)	A_c (Å ²)	ΔG_m° (kJ mol ⁻¹)
	Surface tension	Conductivity					
PMQ-I ^b	2.51	3.64	38.4	2.33	1.48	172	–38.2
PMQ-IV ^b	2.24	3.41	38.9	2.30	1.80	93	–38.7
PMQ-VI ^b	1.45	3.00	37.9	2.49	1.83	91	–40.9
PMQ-VI ^c	1.48	3.20	37.9	2.70	1.72	97	–40.8
PDQ-I ^b	3.48	4.69	39.5	2.25	0.97	171	–36.5
PDQ-II ^b	1.82	3.75	38.0	2.45	1.18	140	–39.7
PDQ-III ^b	3.64	2.73	38.3	2.17	1.10	152	–36.3

^a See text for interpretation of symbols

^b 1.88 M aqueous ethanol

^c 0.37 M aqueous ethanol

addition of ethanol, together with data for PDQ-VI in water at neutral pH are shown in *Figure 1*. The results for all polymerizable and non-polymerizable monoquaternary ammonium cationic surfactants at 25°C in water at neutral pH are shown in *Table 1*. Some corresponding data obtained at pH 2.2 appears in *Table 2*, while the effect of ethanol (1.88 M in water) as an additive is illustrated by the data in *Table 3*. Corresponding data for all the polymerizable and non-polymerizable

di-quaternary ammonium cationic surfactants at 25°C in water at neutral pH are summarized in *Table 5*.

Electrical conductivity method. The required data was obtained as previously reported³ using a simple dip cell and a Wayne Kerr Bridge (Type B224) operating at 1000 Hz. Previously we have converted observed conductivity, G , corrected for the small observed conductivity of doubly distilled water, G_o , into specific conductivity, S

Table 4 Surface activity data^a for PMQ-VII and PMQ-VIII derived from surface tension measurements at 25°C in water

Surfactant	Pre-plateau region ^b		Post-plateau region ^c	
	$\Gamma_{\max} \times 10^6$ (mol m ⁻²)	A (Å ²)	$\Gamma_{\max} \times 10^6$ (mol m ⁻²)	A (Å ²)
PMQ-VII	0.25	659	2.29	73
PMQ-VIII	0.30	551	2.14	78

^a See text for interpretation of symbols

^b Concentration region below plateau seen in $\gamma/\log C$ plot

^c Concentration region above plateau seen in $\gamma/\log C$ plot

(= $KG \text{ ohm}^{-1} \text{ cm}^{-1}$, where K is the cell constant), and thence to molar conductivity, λ (= $SV \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, where V = volume in cm^3 containing one mole of ionic species). In the present work, however, estimation of cmc from λ vs (concentration)^{1/2} plots proved to be very inaccurate, and instead plots of S vs concentration

were exploited. These show clear inflection points as illustrated by the data for PMQVI in Figure 2.

Tables 1, 2, 3 and 5 summarize the results obtained from the conductivity experiments.

Emulsion polymerizations. Typically surfactant (0.3 g), azobisisobutyronitrile (0.01 g) and monomer (1 g) (either styrene or methyl methacrylate) were added to deionized water (10 ml). After vigorous shaking a stable white emulsion was formed and this was heated at 80°C for 24 h. Stable polymer latex was so formed and was used directly for stability studies.

Polymer emulsion stability studies. Samples (1 ml) of each polymer latex were pipetted into test tubes and various electrolyte solutions (1 ml) were then added. The electrolytes used contained mono-, di- and tri-valent metal cations and appropriate anions at concentrations of 1 and 5 M (or saturated solutions if water solubility

Table 5 Surface activity data^a for polymerizable and non-polymerizable diquaternary ammonium cationic surfactants at 25°C in water

Surfactant	Critical micelle concentration $\times 10^2$ (M)		γ_{cmc} (mN m ⁻¹)	pC ₂₀	$\Gamma_{\max} \times 10^6$ (mol m ⁻²)	A (Å ²)	ΔG_m° (kJ mol ⁻¹)
	Surface tension	Conductivity					
PDQ-I	1.23	2.16	38.2	2.61	1.15	145	-41.7
PDQ-II	0.98	2.57	38.9	2.71	1.11	151	-42.8
PDQ-III	2.56	1.72	40.0	2.23	1.11	150	-38.1
PDQ-IV	0.87	2.92	37.9	2.71	1.29	129	-43.5
PDQ-V	2.26	2.67	41.4	2.33	1.04	161	-38.7
PDQ-VI	1.41	3.24	41.5	2.35	1.12	149	-41.0
DQ-I	4.47	-	36.8	1.89	1.64	101	-35.3
DQ-II	2.88	-	37.2	2.09	1.54	108	-37.5
DQ-III	0.36	-	44.4	2.75	1.34	124	-47.7
DQ-IV	2.32	-	37.1	2.43	1.42	117	-38.6
DQ-V	4.45	2.71	37.6	1.77	1.29	128	-35.3

^a See text for interpretation of symbols

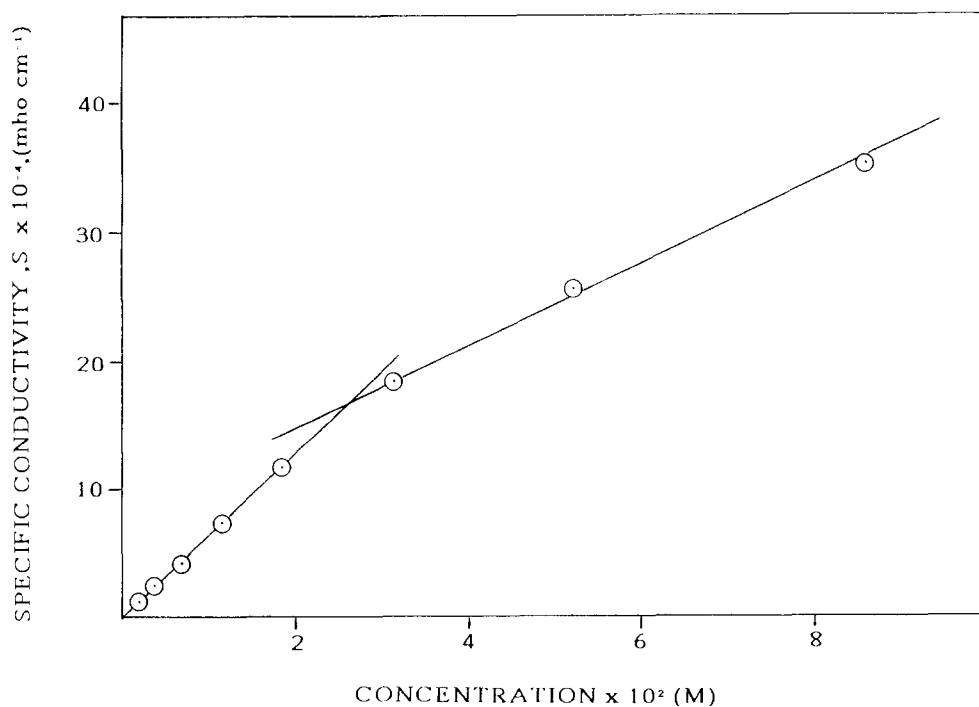

Figure 2 Specific conductance, S , vs concentration plot for PMQ-VI

Table 6 Results of stability tests on emulsion polymers^a prepared with polymerizable monoquaternary ammonium cationic surfactants and their non-polymerizable analogues

Surfactant	Emulsion polymer	Appearance of emulsion after standing for 3 months	Appearance of emulsion after shaking with salt solutions	Appearance of emulsion after addition of salt solutions and on standing for one week	Appearance of emulsion after freeze-thaw cycling
PMQ-I	S	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-I	MM	Emulsion	Some pptn. for all salt solutions	Some pptn. for all salt solutions	Emulsion
PMQ-II	S	Emulsion	Some pptn. with sat. NaCl and sat. AlCl ₃	Some pptn. with sat. NaCl and sat. AlCl ₃	Emulsion
PMQ-II	MM	Emulsion	Some pptn. for all salt solutions	Some pptn. for all salt solutions	Emulsion
PMQ-III	S	Emulsion	Some pptn. for all salt solutions	Some pptn. for all salt solutions	Emulsion
PMQ-III	MM	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-IV	S	Emulsion	Some pptn. with NaCl and 1 M CaCl ₂	Some pptn. with NaCl and 1 M CaCl ₂	Emulsion
PMQ-IV	MM	Emulsion	Two layers with NaCl and 1 M CaCl ₂	Two layers with NaCl and 1 M CaCl ₂	Emulsion
PMQ-V	S	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-V	MM	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-VI	S	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-VI	MM	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-VII	S	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-VII	MM	Emulsion	Emulsion	Emulsion	Emulsion
PMQ-VIII	S	Emulsion	Some pptn. with sat. NaCl and sat. AlCl ₃	Some pptn. with sat. NaCl and sat. AlCl ₃	Sedimentation
PMQ-VIII	MM	Emulsion	Emulsion	Sedimentation with 1 M NaCl, two phases with sat. NaCl	Emulsion
MQ-I	S	Emulsion	Emulsion	Some sedimentation with all salt solutions	Emulsion
MQ-I	MM	Emulsion	Emulsion	Emulsion	Emulsion
MQ-II	S	Emulsion	Emulsion	Some pptn. with NaCl and sat. Na ₃ PO ₄	Emulsion
MQ-II	MM	Emulsion	Emulsion	Emulsion	Emulsion
MQ-III	S	Emulsion	Some pptn. with sat NaCl, sat. AlCl ₃ , and sat. Na ₂ SO ₄	Some pptn. with all salt solutions	Sedimentation
MQ-III	MM	Emulsion	Some pptn. with all salt solutions. Sedimentation with sat. NaCl	Some pptn. with all salt solutions. Sedimentation with sat. NaCl	Emulsion
MQ-IV	S	Emulsion	Emulsion	Emulsion	Emulsion
MQ-IV	MM	Emulsion	Emulsion	Emulsion	Emulsion
MQ-V	S	Emulsion	Emulsion	Emulsion	Emulsion
MQ-V	MM	Emulsion	Emulsion	Emulsion	Emulsion

^a See Experimental section for details of emulsion polymerization conditions and stability tests

^b S = styrene polymer; MM = methyl methacrylate polymer

was low). The salts used were: sodium chloride, sodium sulphate, tri-sodium orthophosphate, calcium chloride and aluminium chloride hexahydrate. The stability of emulsions was assessed visually immediately after shaking with electrolyte solutions and after further standing for one week. For comparison, uncontaminated emulsions were also left for 3 months and then examined visually.

Each latex sample was also subjected to a freeze-thaw cycle. Again visual observation of stability was made one day later and after a further period of one week.

The results of these observations are summarized in Tables 6 and 7.

DISCUSSION

Micellization of monoquaternary ammonium cationic surfactants

The polymerizable species PMQ-I–VI and the non-polymerizable models MQI-V all displayed a critical

micellization phenomenon. The cmc for CTAB (Table 1) agrees well with our own previously determined values⁷ and with other data in the literature^{33,34}, and so both our surface tension and electrical conductivity methodologies seem sound within an error of $\sim \pm 5\%$. The agreement in cmc data from surface tension and conductivity measurements is less good for the novel surfactants. The latter do possess headgroups of a relatively complex and diverse nature (relative to simple surfactants) and this factor may be of relevance in this context. The monoquaternary ammonium salts PMQ-VII and PMQ-VIII failed to show any discrete transition and this was expected bearing in mind the short hydrocarbon chain in these molecules ($(\text{CH}_2)_6$). Their surface tension behaviour will be discussed in more detail later.

The cmc values (Table 1) for MQI-III (and likewise the diquaternary ammonium ion analogues DQI-III) (Table 5) show the expected trend to lower values as the length of the hydrocarbon tail increases $\text{C}_{10} \rightarrow \text{C}_{12} \rightarrow \text{C}_{16}$ with the data for MQ-III conforming

Table 7 Results of stability tests on emulsion polymers^a prepared with polymerizable diquaternary ammonium cationic surfactants and their non-polymerizable analogues

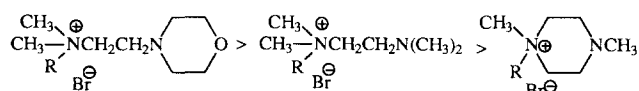
Surfactant	Emulsion polymer	Appearance of emulsion after standing for 3 months	Appearance of emulsion after shaking with salt solutions	Appearance of emulsion after addition of salt solutions and on standing for one week	Appearance of emulsion after freeze-thaw cycling
PDQ-I	S	Emulsion	Some pptn. with sat. NaCl and sat. AlCl ₃	Some pptn. with sat. NaCl and sat. AlCl ₃	Emulsion
PDQ-I	MM	Emulsion	Emulsion	Emulsion	Emulsion
PDQ-II	S	Emulsion	Some pptn. with all salt solutions	Two layers	Emulsion
PDQ-II	MM	Emulsion	Some pptn. with sat. NaCl and sat. AlCl ₃	Some pptn. with sat. NaCl and sat. AlCl ₃	Emulsion
PDQ-III	S	Emulsion	Some pptn. with all salt solutions. Two layers with sat. NaCl ₃	Some pptn. with all salt solutions. Two layers with sat. NaCl ₃	Sedimentation
PDQ-III	MM	Emulsion	Some pptn. with all salt solutions. Two layers with sat. CaCl ₂	Some pptn. with all salt solutions. Two layers with sat. CaCl ₂	Emulsion
PDQ-IV	S	Emulsion	Emulsion	Some pptn. with sat. CaCl ₂ , sat. AlCl ₃ , sat. and 1 M Na ₂ SO ₄	Emulsion
PDQ-IV	MM	Emulsion	Emulsion	Sedimentation for all salt solutions	Emulsion
PDQ-V	S	Emulsion	Emulsion	Some pptn. for all salt solutions	Emulsion
PDQ-V	MM	Emulsion	Emulsion	Some pptn. for all salt solutions	Emulsion
PDQ-VI	S	Emulsion	Some pptn. for all salt solutions	Some pptn. for all salt solutions	Emulsion
PDQ-VI	MM	Emulsion	Emulsion	Some pptn. for all salt solutions	Emulsion
DQ-I	S	Emulsion	Emulsion	Emulsion	Emulsion
DQ-I	MM	Emulsion	Emulsion	Emulsion	Emulsion
DQ-II	S	Emulsion	Emulsion	Emulsion	Emulsion
DQ-II	MM	Emulsion	Emulsion	Emulsion	Emulsion
DQ-III	S	Emulsion	Emulsion	Emulsion	Emulsion
DQ-III	MM	Emulsion	Some pptn. sat. NaCl and with sat. AlCl ₃	Some pptn. sat. NaCl and with sat. AlCl ₃	Emulsion
DQ-IV	S	Emulsion	Some pptn. with sat. AlCl ₃	Some pptn. with sat. AlCl ₃	Emulsion
DQ-IV	MM	Emulsion	Some pptn. with sat. AlCl ₃	Some pptn. with sat. AlCl ₃	Emulsion
DQ-V	S	Emulsion	Emulsion	Emulsion	Emulsion
DQ-V	MM	Emulsion	Emulsion	Some pptn. with all salt solutions	Emulsion

^a See Experimental section for details of emulsion polymerization and stability tests

^b S = styrene polymer; MM = methyl methacrylate polymer

closely to that of CTAB. Generally the cmc values for PMQ-I–VI are very similar to each other approximating to that for say C₁₄H₂₉N[⊕](CH₃)₃Br. Since the hydrocarbon chain in these molecules is -(CH₂)₁₁, the more complex headgroups and the ester substituents in the tail, contribute to an increase in overall hydrophobicity relative to say C₁₁H₂₃N[⊕](CH₃)₃Br. The cmcs of the methacrylate esters are consistently a little lower than those of the corresponding acrylates, confirming that the α-methyl substituent increases the overall hydrophobicity of the surfactant. The data for the dicationic species PDQ-I–VI (Table 5) show the same trend.

For the monocationic groupings: PMQ-I, PMQ-III and PMQ-V; PMQ-II, PMQ-IV and PMQ-VI; and MQ-II, MQ-IV and MQ-V there is close correlation with the effect on cmc of the structure of the headgroup. In general the cmc (Table 1) increases in the order



This suggests that the hydrophilicity of these groups increases in this manner as well, with the morpholine derivative being the most hydrophilic. This group may be able to interact more strongly with water molecules, via H-bonding, disfavoring micelle formation. The same trend has been reported before for decylpiperidinium bromide and decylmorpholinium bromide³⁵.

Overall the cmc values here are, however, lower than those reported for structurally similar acrylated and methacrylated surfactants with simple trimethylammonium and pyridinium bromide headgroups^{3,12}. The more complex headgroups in the present work are all therefore somewhat more hydrophobic than the simple ones and this result seems very reasonable.

Air/water interfacial behaviour of monoquaternary ammonium cationic surfactants

γ_{cmc} is one measure of the effectiveness of a surfactant and the values for the monoquaternary ammonium salts here lie in a narrow range, ~35.5–40.00 mN m⁻¹ (Table 1), very comparable to the data already reported for similar surfactants²³. For a given structure in the

hydrophobic tail, surfactants with the morpholine residue in the headgroup showed the highest γ_{cmc} values, again probably reflecting the slightly stronger interaction of this headgroup with water. In general, the effectiveness of surfactants with different headgroups in reducing γ_{cmc} correlates with their hydrophobicity deduced from cmc data, i.e. the effectiveness is in the reverse order to that shown above for cmc.

The parameter $\text{p}C_{20}$ is the negative logarithm of the concentration of surfactant required to reduce the surface tension of water by 20 mN m^{-1} and is another convenient measure of the efficiency of a surfactant³⁶. The higher the value the greater is the tendency for the surfactant to absorb at the air/water interface. Again there is good correlation (*Table 1*) with surfactant headgroup structure, analogous to that for γ_{cmc} .

Application of the Gibb's adsorption isotherm for 1/1 electrolytes³⁷ allows the surface excess concentration Γ_{max} (mol m^{-2}), and the area occupied per surfactant molecule at the air-water interface, A (\AA^2), to be calculated from the gradient of each surface tension - log (concentration) plot at the cmc.

$$\Gamma_{\text{max}} = \frac{-1}{n \times 2.303RT} \left(\frac{d\gamma}{d \log C} \right)_{\text{T}}$$

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

where R = gas constant, N_{A} = Avogadro's number, $n = 2$ for 1/1 electrolytes, and $n = 3$ for 2/1 electrolytes.

The free energy of micellization, $\Delta G_{\text{m}}^{\circ}$, can also be estimated to a first approximation from

$$\Delta G_{\text{m}}^{\circ} = nRT \ln \chi_{\text{cmc}}$$

where χ_{cmc} is the concentration of surfactant at the cmc expressed in mole fraction units. This does assume however that the association can be treated as 'closed' and that the micelles have a moderately large association number. The data derived are shown in *Tables 1-5*.

For the polymerizable monoquaternary ammonium salts PMQ-I-VI the values of A lie in the range ~ 105 to 115 \AA^2 except for PMQ-II which is a little larger. The values for CTAB and DDTAB are 95 and 73 \AA^2 respectively probably reflecting the more compact headgroup of these species. The values for the non-polymerizable species MQI-V lie in the range $\sim 75-120 \text{ \AA}^2$.

The $\Delta G_{\text{m}}^{\circ}$ values of PMQ-I-VI lie in the narrow range $\sim 42-47 \text{ kJ mol}^{-1}$, with PMQ-V and PMQ-VI, both possessing the more hydrophilic morpholine substituted headgroup, predictably having the lower negative values. The data for the group MQI-II also correlate well with structure. As the hydrocarbon chain is increased $C_{10} \rightarrow C_{12} \rightarrow C_{16}$ then $\Delta G_{\text{m}}^{\circ}$ becomes progressively more negative reflecting the increase in hydrophobicity, and in the tendency to micellize.

Effect of pH and ethanol additive on surface activity

Surface activity data for the polymerizable monoquaternary ammonium salts PMQ-I-VI are shown in *Table 2*. It was thought at $\sim \text{pH } 2$ the second (neutral) amine group in these molecules would be substantially protonated, significantly increasing the overall hydrophilicity of each surfactant and generating in effect dicationic headgroups. It was expected therefore that cmc values would rise, and that charge repulsion between headgroups would also be higher. Indeed, this does seem to be so, in all cases the cmc does rise, the effect being

more pronounced with PMQ-V and PMQ-VI. The situation is not entirely clear-cut, however, because the acid used in adjusting the pH was HCl, and so some exchange of Br^{\ominus} and Cl^{\ominus} is likely at low pH. Br^{\ominus} is more easily polarized than Cl^{\ominus} and so is able to shield adjacent charges on surfactants within a micelle more effectively. This favours micelle formation and so the cmcs of surfactants with a Br^{\ominus} counterion are lower than those of analogous species with a Cl^{\ominus} counterion. The rise in cmc at low pH may therefore have some origin in an exchange of the counterion.

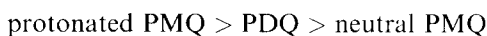
Changes in the other parameters γ_{cmc} and $\text{p}C_{20}$ are rather small but not inconsistent with the protonation of the headgroups at low pH. The increase in the A values is perhaps the most significant effect. This can be rationalized in terms of increased charge repulsion between the dicationic headgroups of surfactants in the air/water monolayer and possibly in terms of the conformation of the headgroup. This point is dealt with more fully later with the diquaternary ammonium ion surfactants.

The effect of addition of ethanol on the surface activity properties of PMQ-I, PMQ-IV and PMQ-VI is shown in the data in *Table 3*. In all cases the cmc rises as reported already in the literature^{38,39} for other surfactants. The simplest explanation for this is simply a modest increase in the solubility of the surfactant in the presence of ethanol. The dicationic species PDQI-III behave similarly (*Table 3*) and these changes might be important, e.g. in formulating emulsion polymerizations when an alcohol component might be present. The changes in the value of A are interesting. For PMQ-I and PDQ-I there is a significant rise, while for the other species the change is rather small, and generally a decrease. This suggests that there is a specific effect of headgroup in PMQ-I and PDQ-I with regard to its interaction with ethanol but what this might be is not clear to us.

Micellization and interfacial behaviour of diquaternary ammonium cationic surfactants

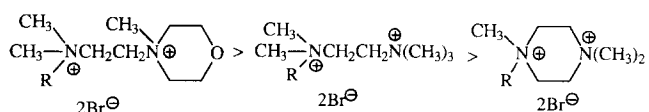
Table 5 summarizes all the surface activity data for the dicationic species PDQ-I-VI and DQ-I-V. The cmc values for all of these are higher than the values for the corresponding monocationic species (*Table 1*). This is as expected bearing in mind the overall higher hydrophilicity of the dicationic molecules and the likely increase in charge repulsion between adjacent headgroups in a micelle. The methacrylate derivatives have lower cmcs than their acrylate analogues as observed for the monocationic salts. The rather large increase for acrylate PDQ-III over acrylate PMQ-III seems anomalous and we can offer no reasonable explanation. An increase in cmc of divalent surfactants over analogous monovalent species has been observed before⁴⁰. Shinoda⁴¹ has studied a series of potassium alkyl malonates with the general formula $\text{CH}_3(\text{CH}_2)_n\text{CH}(\text{COOK})_2$ and Hagslatt *et al.*⁴² have synthesized and investigated the properties of the divalent quaternary ammonium salt, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^{\oplus}\text{Cl}^-$. The latter has a cmc of $\sim 3.3 \times 10^{-2} \text{ M}$, somewhat higher than the range found here for our divalent species $\sim 0.9-2.3 \times 10^{-2} \text{ M}$, but comparable to the values for DQ-IV and DQ-V. This bis-hydrochloride salt of Hagslatt *et al.*⁴² would, of course, be expected to be more hydrophilic than fully alkylated ammonium salts in the present work. Perhaps of more relevance to our use of these

polymerizable amphiphiles in emulsion polymerizations is the relative values of the cmc of a given monoquaternary ammonium salt, its protonated analogue at low pH (now a dicationic species) and the analogous methylated diquaternary ammonium salt. In all cases except PMQ-I/PDQ-II the value of the cmc rises in the sequence:



Thus, both dicationic species have higher cmcs than the monocationic but the *protonated* dicationic species is significantly more hydrophilic than the *methylated* dicationic, and has the highest cmc.

As with the polymerizable mono-quaternary ammonium bromides, for a given surfactant tail structure, the cmc increases with headgroup structure in the sequence



Again this seems to reflect the relative hydrophilicity of these structures and the picture is self-consistent across the monocationic and the dicationic species.

Of the other data the values of A are worth highlighting. These are generally higher than their monocationic analogues and as with the protonated monocationics this can be rationalized in terms of increased charge repulsion between the dicationic headgroups of surfactants in the air/water monolayer. There

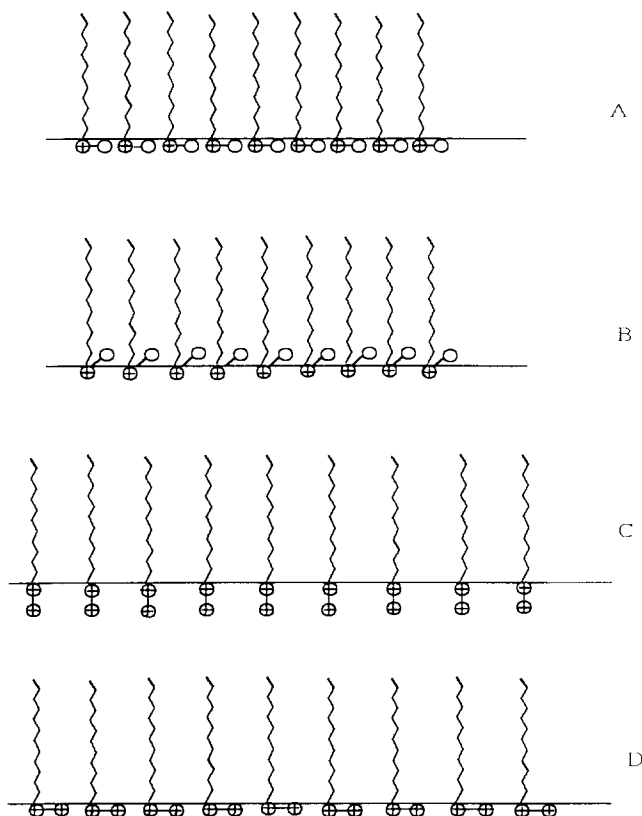


Figure 3 Schematic representation of possible packing arrangements for MQ species (A and B) and DQ species (C and D) at air-water interface: A, monoquaternary ammonium species with uncharged headgroup component in water phase; B, monoquaternary ammonium species with uncharged headgroup component out of water phase; C, D, diquaternary ammonium species with double charges orientated perpendicular to and parallel to the interface respectively

may also be a contribution from a change in local conformation of the headgroup. The monocationic species may be able to use the uncharged polar structural component of the headgroup ($-\text{O}$) to help shield positive charges ($-\oplus$) from each other. It is not even clear where this part of the headgroup is located (in the water phase or outside?) (Figure 3A, B). In the case of the dicationic species undoubtedly both charges are solvated within the aqueous phase but the precise orientation of these to minimize charge repulsion again is unknown (Figure 3C, D). Overall, however, each surfactant molecule of the latter type occupies a larger area than the monocationic.

Interfacial behaviour of the short chain polymerizable amphiphiles PMQ-VII and PMQ-VIII

These two molecules were synthesized in the expectation that they would *not* exhibit micellization (see later) and this indeed proves to be the case. No clear cmc transition is observed in their surface tension/concentration behaviour. However, the molecules are surface active and their surface tension/log (concentration) plots are very curious (Figure 4). In both cases increasing concentration of the salt lowers the surface tension but around $\sim 5 \times 10^{-3} \text{ M}$ a discrete plateau region emerges. Further increase in the concentration causes a rapid fall in the surface tension apparently towards a cmc, but the systems phase separate before a clear-cut micellar region is entered. Although highly speculative it is possible to use the Gibb's adsorption isotherm to obtain a possible value for the surface area occupied per molecule on approaching the plateau region (from low concentration). Likewise, a second value can be deduced from the steep curve after the plateau region. The data are shown in Table 4. The values of A beyond the plateau region are very close to those of species like DDTAB (Table 1). Thus it seems reasonable to suggest that PMQ-VII and PMQ-VIII pack more or less vertically at the air-water interface in this concentration range similarly to other surfactants (Figure 5A). The interpretation of the levelling of the surface tension in the plateau region is more difficult but it does suggest some ordering of molecules at the surface generating an environment less polar than water, but overall not as non-polar as a hydrocarbon. The calculated average surface area occupied per molecule assuming the Gibb's adsorption isotherm is applicable is very large $\sim 500\text{--}600 \text{ \AA}^2$. This only seems possible if these molecules lie 'full-length' in the surface (Figure 5B). Weak electrostatic interaction of the terminal $\text{N}^+(\text{CH}_3)_3$ and carbonyl ester groups might serve to give the array some stability (Figure 5C). Why should such arrangements arise with these C_6 hydrocarbon structures and not with more conventional surfactants with larger hydrophobes? One possibility is that the latter offer a 'quantum' of hydrophobicity which is too large, and even dilute gatherings of these molecules quickly form islands with the hydrophobes aggregated clear of the aqueous phase. With PMQ-VII and PMQ-VIII there is also polarity at both ends of each molecule to anchor these in a flat conformation on the surface. Previous work with similarly terminally substituted surface active species has shown anomalous surface tension behaviour⁴³ and the possibility of various 'looped' conformations in the surface⁴⁴. Clearly these models and the treatment of the experimental data are highly speculative, but they do offer a challenge to

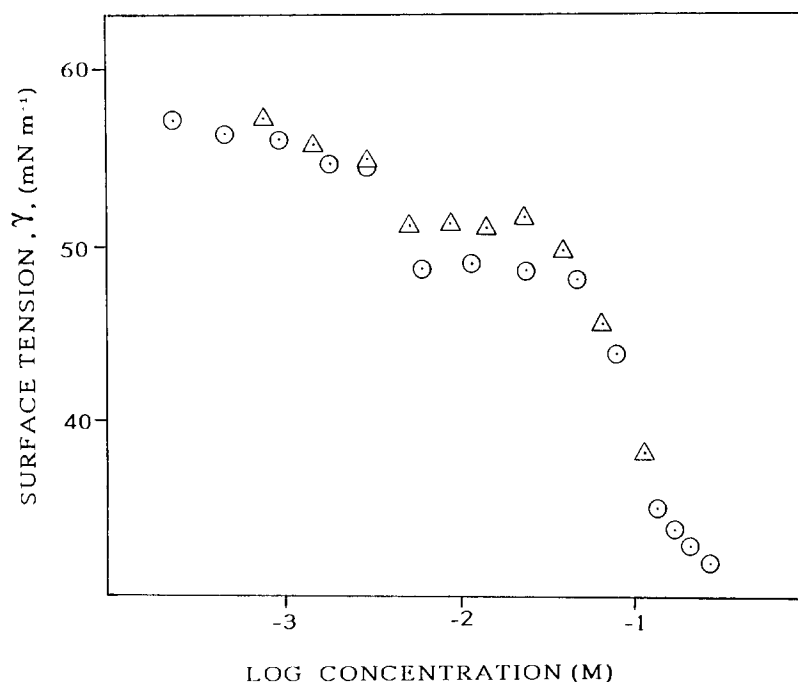


Figure 4 Surface tension, γ , vs log concentration plots for: Δ , PMQ-VII; \circ , PMQ-VIII (short chain species)

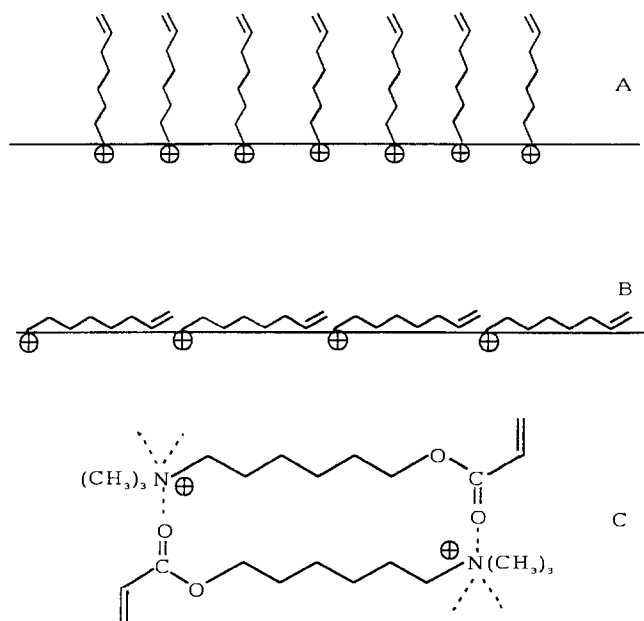


Figure 5 Possible packing arrangements for PMQ-VII and VIII at the air-water interface: A, in the post-plateau $\gamma/\log C$ region; B, in the pre-plateau $\gamma/\log C$ region; C, possible electrostatic interactions between cationic headgroups and polar ester carbonyl groups contributing to stability of packing arrangement B

surface physical chemists perhaps to undertake more detailed studies of these and similar molecules.

Interfacial behaviour of polymerized diquaternary ammonium cationic surfactants

The polymerizable surfactants under study here were produced primarily for use in emulsion polymerizations. However, homopolymerization of these species³⁰ in isotropic solution is a potential route to polymeric surfactants in which there is also much interest at the moment. Polymeric surfactants which form unimolecular (intramolecular) micelles from *individual* polymer

chains might be expected to do so at all concentrations above zero. They would not therefore be expected to show a cmc (i.e. $\text{cmc} = 0$). This was found to be the case for the polymers from PDQ-I and PDQ-II studied in this work. The surface tension-concentration behaviour of these polymers and their precursor monomers is shown in Figure 6. The two monomers display a typical cmc effect, but their polymers though reducing the surface tension do so only modestly, and without any indication of forming a new stable (pseudo) phase. This behaviour can be rationalized in terms of spontaneous formation of unimolecular micelles at all concentrations. Such micelles would be located largely in the bulk of the aqueous phase, and so the polymer, though surface active, would not be available for packing at air/water interface and would not therefore progressively reduce the surface tension. This contrasts with the earlier results from our laboratory with polymerized nonionic surfactants¹⁵ where the polymers were found to display cmc behaviour. In the latter case, however, the 'polymers' were in fact only oligomers (maximum degree of polymerization ~ 10) and the micellization phenomenon seems to involve aggregation of these oligomers, which *individually* are too small to form unimolecular micelles. Attempts to measure the molecular weights of the polymers from PDQ-I and PDQ-II proved futile. Their polycationic nature, coupled with their surface active properties, seem to offer the worst possible characteristics for application of classic molecular weight determination methods.

Emulsion polymerizations and latex stability tests

The surfactant used in an emulsion polymerization plays a number of roles. Perhaps the two key ones are: to control the complex physical phase behaviour of the polymerizing mixture so that stable emulsion polymer particles are formed, and secondly, to maintain the physical stability of the so-formed polymer latex until such time as the emulsion is ready for destabilization and

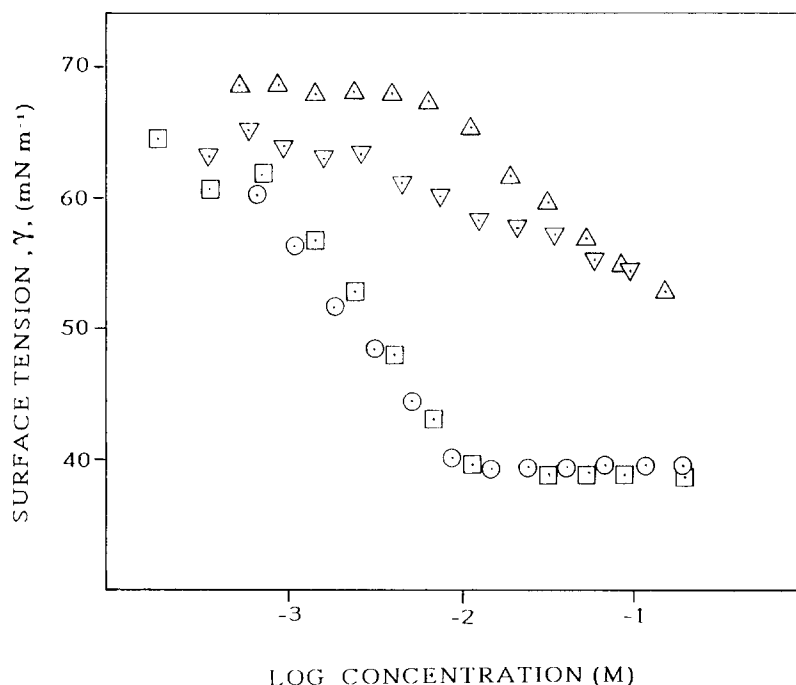


Figure 6 Surface tension, γ , log concentration plots for: Δ , polymer of PDQ-I; ∇ , polymer of PDQ-II; \square , PDQ-I; \circ , PDQ-II

exploitation, e.g. in film-forming. Paradoxically in many instances once the emulsion is exploited the role of the surfactant is not only complete, but its very presence can be detrimental in the final application, e.g. emulsion paints, even after prolonged application retain moisture sensitivity, especially when coupled with mild abrasion. Presumably a primary source of weakness here is the residual (partially hydrophilic) surfactants. Recently a potentially novel solution to this problem has emerged from the author's laboratory in the form of photolabile surfactants⁴⁵. These amphiphiles are cleaved on exposure to light generating a hydrophobe and small salt fragments. The latter in say an applied external paint, might be gradually 'weather washed' away, i.e. the degree of hydrophobicity of such a film would increase on weathering. Such potential technology needs much more development yet.

In contrast, the use of polymerizable surfactants in emulsion or dispersion polymerizations has been exploited for some time^{17,20,36,46,47}. Copolymerization of the surfactant onto the surface of an emulsion polymer particle might be expected to increase emulsion stability by permanently fixing of the headgroups and at least prevent *migration* of the surfactant in say a finished paint film, without entirely removing the hydrophilic component of its nature. Despite the general perception that polymerizable surfactants might bring these advantages, demonstrating unambiguously, for example, improved latex stability in *simple model systems* has proved very difficult to achieve. Our earlier work with polymerizable monocationic surfactants with the polymerizable moiety either in the headgroup or at the tail-end was not encouraging⁷. Likewise emulsions prepared with a range of polymerizable nonionic surfactants¹⁵ proved to be less stable than those prepared with structurally analogous conventional nonionic amphiphiles. Possible deficiencies with the latter species were: (i) the polymerizable group was attached to the terminus of the hydrophilic headgroup, and (ii) efficient copolymerization of the surfactant may result in incorporation of

significant quantities within the interior of emulsion particles, rather than concentrating at the surface as required for maximum stability. Both of these factors are currently under investigation in the author's laboratory in collaboration with other European laboratories⁴⁸. The observations by Tauer *et al.*⁴⁹ that a maleate-based surfactant results in a remarkable enhancement of emulsion stability, and that the limited reactivity of this species encourages polymerization largely on the surface of particles, tend to confirm that our thinking is sensible.

The PDQ-I–VI surfactants in the present work were designed to prove the naive view that increasing the charge density on emulsion polymer particles should increase latex stability, and binding the charges to the surface via copolymerization should further enhance the effect. Surfactants DQ-I–V are non-polymerizable dicationic analogues to provide a basis for comparison, and likewise the polymerizable mono-cationics PMQ-I–VI and their non-polymerizable analogues MQ-I–V were to provide as direct a structural comparison as possible with singly charged amphiphiles. Small-scale batch emulsion polymerizations of styrene and methyl methacrylate using a monomer:water ratio of $\sim 1/10$ and an aqueous phase of $\sim 3\%$ surfactant yielded stable emulsions with essentially no discrimination between the surfactants employed. In all cases the emulsions remain stable after standing at room temperature (Tables 6 and 7).

Generally the behaviour of the styrene and methyl methacrylate emulsions was very similar with perhaps the latter showing marginally better stability. Few emulsions, for example, flocculated in the freeze-thaw test, but the 3 out of 48 that did were all styrene-based latexes. Comments about the performance of specific surfactants are therefore based upon their average behaviour with both monomer systems.

Considering all the polymerizable species, acrylates and methacrylates behaved similarly except in the case of PMQ-VII and PMQ-VIII where the acrylated species yielded significantly more stable emulsions.

Comparing dicationic with monocationic headgroups is complex since the results are headgroup structure dependent. With the non-polymerizable species there is a clear trend that the dicationics DQ-I–III yield more stable emulsions than their monocationic analogues MQ-I–III. In both groups performance declines as the hydrophobicity increases (cmc decreases), with PQ-III and MQ-III being the least effective stabilizers in each group. With the more complex headgroups, however, the monocationics MQ-IV and MQ-V provide better stability than the dicationics DQ-IV and DQ-V. In the case of the two polymerizable series PMQ-I–VI and PDQ-I–VI there is little to choose in terms of monocationic vs dicationic. Certainly the latter provide no clear increase in stability, indeed the balance tends to be in favour of the monocationics.

Regarding performance of polymerizable vs non-polymerizable species of closely analogous structure again no uniform picture emerges, there is a significant dependence on the structure of the headgroup. For $-\text{N}^{\oplus}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{Br}^{\ominus}$, polymerizable and non-polymerizable species in general behave similarly, the influence of chain length in MQ-I–III is by far the most significant factor. For the monocationic headgroup $-(\text{CH}_3)\text{N}^{\oplus}\text{N}^{\oplus}\text{CH}_3\text{Br}^{\ominus}$ the non-polymerizable species MQ-IV is the most effective, whereas for the monocationic headgroup $-\text{N}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{N}^{\oplus}\text{OBr}^{\ominus}$ the polymerizable species PMQ-V and PMQ-VI are particularly effective. For the dicationic headgroup $-\text{N}^{\oplus}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{N}^{\oplus}(\text{CH}_3)_2\text{Br}^{\ominus}$ the non-polymerizable species DQ-I–III generally provide better stability than the polymerizable ones PDQ-I and PDQ-II. For the other dicationic headgroups $-(\text{CH}_3)\text{N}^{\oplus}\text{N}^{\oplus}(\text{CH}_3)_2\text{Br}^{\ominus}$ and $-(\text{CH}_3)_2\text{N}^{\oplus}\text{CH}_2\text{CH}_2(\text{CH}_3)\text{N}^{\oplus}\text{O}_2\text{Br}^{\ominus}$ non-polymerizable and polymerizable analogues generally behave similarly.

The two polymerizable monocationic species PMQ-VII and PMQ-VIII were designed to test a quite separate hypothesis and, in particular, to try to probe the issue of whether improving the localization and binding of charge to the surface, as opposed to partial loss to the interior of particles, improves latex stability. The idea was to develop polymerizable amphiphiles *just too hydrophilic* to micellize so that their locus in emulsion polymerizations would be substantially in the aqueous phase (as monomers) offering the maximum opportunity for polymerization on the surface of growing polymer particles. Indeed, these non-micellizing surfactants perhaps somewhat surprisingly do act very satisfactorily as stabilizers in conventional emulsion polymerizations. Although rather outside the coverage of this paper, this does raise an important question about the limits on molecular structure of species capable of functioning as efficient emulsion polymerization stabilizers, and suggests that novel opportunities may exist here. Not only do PMQ-VII and PMQ-VIII yield stable emulsions, but those from acrylate species PMQ-VII are as stable as any of the other emulsions produced in this work. Unfortunately our test protocols are not sufficiently sensitive to say that PMQ-VII is a superior species in this respect to the others, but the results do show that structures such as these are worthy of further study, and that the strategy of trying to ensure *surface binding* of charges is well worth pursuing.

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