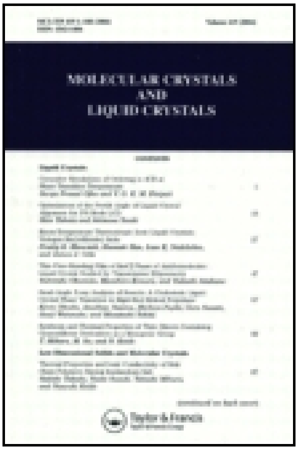

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Thermotropic Liquid Crystalline Character and Vesicular Properties of Some Functionalized Long-Chain Di-*n*-dodecyl Quaternary Ammonium Salts

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In several reports it has been shown that amphiphilic molecules, including phospholipids, which aggregate in solution to form micelles, vesicles or liposomes also exhibit thermotropic liquid crystalline phases. In conjunction with our recent work on the synthesis and characterization of vesicle-forming monomeric and polymerized allyl and diallyl di-*n*-alkyl quarternary ammonium salts, a series of analogously functionalized derivatives has been prepared. Di-*n*-dodecyldimethyl quarternary ammonium bromide was employed as the parent compound. The new quarternary ammonium salts were formed by replacing one or both of the methyl groups in the parent compound by groups such as $—CH_2—CH{=}CH_2$, $—CH_2CH_2OH$, $—CH_2COOH$, $—CH_2CH_2COOH$, or $—CH_2CH_2CH_2CN$. The existence of liquid crystalline phases in these quarternaries was established by optical microscopy while transition temperatures as well as thermodynamic parameters were determined by DSC. Some of these compounds when dispersed in water and sonicated ultimately formed vesicles the structure of which was observed by electron microscopy. The effect of the various functional groups on the liquid crystalline phase behavior of these compounds exhibits a well defined variation. However, no systematic variation has been observed on the ability of these same functional groups to affect vesicles formation.

Keywords: thermotropic liquid crystals, vesicles, surfactants, quaternary ammonium salts, optical microscopy, differential scanning calorimetry

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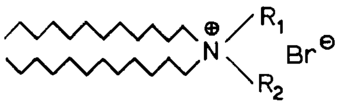
INTRODUCTION

The aggregation of amphiphilic molecules in water to form aggregates such as micelles, vesicles or liposomes is a well-known property.[1] However the exhibition of mesomorphic phases[2–13] by the same compounds although discovered many years ago only recently has been systematically studied.

The smectic or rather the smectic-like character of these compounds, established[13] by their optical textures and x-ray diffraction patterns, results from the chain-melting of the quaternaries which form lamellar structures in the solid phase. Specifically, in the so-formed mesophase, although the alkyl chains have melted, the ionic bonding between polar head and counterions remains practically intact and free molecular motion of the amphiphiles is prevented by the rigidity of the ionic layers in analogy with the behavior in the solid phase. Thus bidimensional polar layers are formed sandwiched between the long alkyl chain layers. In the clearing point the ionic bonds are broken and "isotropic"[13] melts appear.

In connection with our work[14] on the synthesis and characterization of vesicle forming polymerizable allyl and diallyl di-*n*-alkyl quaternary ammonium salts, we have synthesized and characterized the quaternaries shown below in the Scheme. The $R_1 = R_2 = CH_3$ of the parent compound have been replaced by the groups tabulated. In this study the mesomorphic character of these functionalized di-*n*-alkyl quaternaries is established by optical microscopy and differential scanning calorimetry, and it is examined to what extent this mesomorphism is dependent on the functional



Compound	I	$R_1 = —CH_3$	$R_2 = —CH_3$
	II	$R_1 = —CH_3$	$R_2 = —CH_2—CH{=}CH_2$
	III	$R_1 = —CH_2—CH{=}CH_2$	$R_2 = —CH_2—CH{=}CH_2$
	IV	$R_1 = —CH_3$	$R_2 = —CH_2COOH$
	V	$R_1 = —CH_3$	$R_2 = —CH_2CH_2COOH$
	VI	$R_1 = —CH_3$	$R_2 = —CH_2CH_2OH$
	VII	$R_1 = —CH_3$	$R_2 = —CH_2CH_2CH_2CN$

Scheme

group(s). Also the effect of functional groups on the ability of surfactants to disperse and form vesicles in water is studied.

EXPERIMENTAL

Synthesis of di-n-dodecyl quarternary ammonium salts

To 0.01 mole of di-*n*-dodecylmethyl amine or di-*n*-dodecyl-allyl amine dissolved in ethyl acetate are added 0.012 mole of the respective primary bromides i.e. $BrCH_2CH_2OH$, $BrCH_2COOH$, $BrCH_2CH_2COOH$, $BrCH_2CH_2CH_2CN$ and $BrCH_2CH{=}CH_2$. The mixture is stirred several hours for the first four bromides in order for sufficient precipitation of the quaternaries to occur. Allyl bromide on the contrary reacts almost spontaneously with the amines and immediate precipitation of the quarternary salts resulted. Precipitated salts were recrystallized from ethyl acetate and dried over phosphorous pentoxide. Elemental analysis results agreed with the calculated values.

Differential scanning calorimetric diagrams were recorded with a Du Pont 910 DSC equipped with a R90 Temperature Programmer.

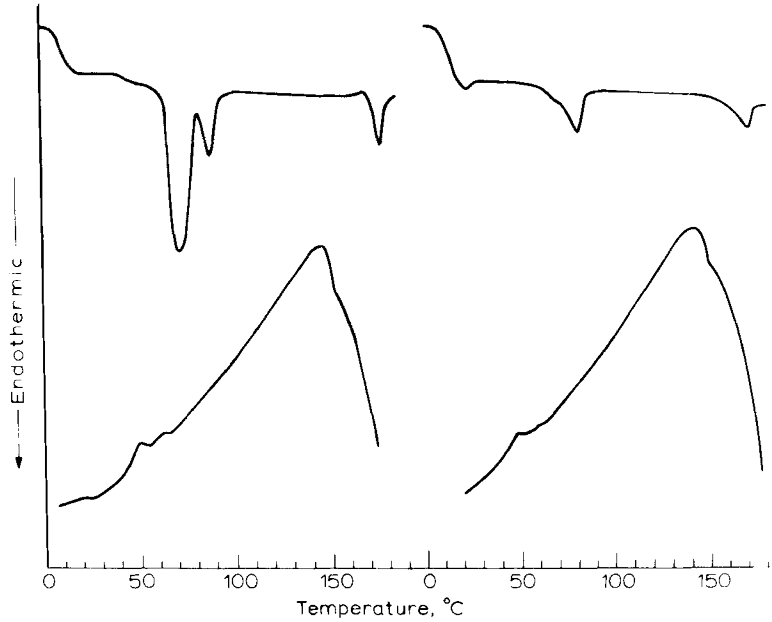
Optical microscopy was performed with a Reichert "Thermopan" polarizing microscope.

For electron microscopy experiments, sonicated dispersions of surfactants were applied on carbon-coated grids and stained with 2% uranyl acetate solution. The grids were examined with a Siemens Elmiscope electron microscope operating at 75 kV.

RESULTS AND DISCUSSION

In an attempt to imitate the bilayer structure of membranes, salts of the general formula $(n\text{-}C_nH_{2n+1})_2MX_4$ were prepared.[8,15] However these compounds can act only as "crystalline models" of bilayer since, to our knowledge, these compounds cannot be dispersed to form lamellar structures or vesicles in solution. On the contrary quaternary salts usually disperse in water. In fact the first synthetic surfactant that was found to form vesicles in water was didodecyldimethyl ammonium bromide[16] (Compound I). This surfactant is characterized as the parent compound in the synthesis of the compounds under investigation. The other compounds were prepared by quaternizing the tertiary amines with the appropriate primary bromide bearing the various functional groups. The quaternization was performed, in general, relatively fast[17] in ethyl acetate in which the quaternaries formed precipitate. Quaternization in this respect affords a facile method for functionalizing the polar head of these surfactants and the only limitation in the synthesis of these compounds is the availability of suitable primary bromides.

The DSC diagrams for two heating-cooling cycles are shown in Figure 1, the transition temperatures as determined by DSC as well as enthalpies and entropies of transition are shown in the Table I. Except for the diallyl derivative which shows only one transition all the other quarternaries show multiple melting behavior. The low temperature main transitions are attributed to the long-chain melting according to the accepted view[13] of amphiphilic compounds having lamellar structure in the solid phase. In compound (I) ($R_1 = CH_3$, $R_2 = CH_3$) the melting transition is followed by a post-melting transition while in compound VII ($R_1 = CH_3$, $R_2 = CH_2CH_2CH_2CN$) the clearing point is preceded by a pre-clearing transition. On the other hand in compound VI ($R_1 = CH_3$, $R_2 = CH_2CH_2OH$) the melting tran-



Compound I

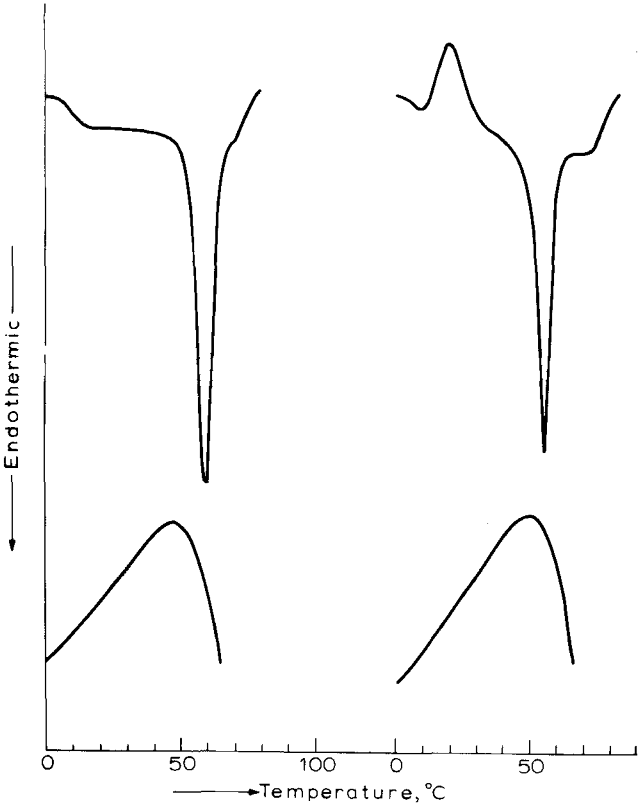
FIGURE 1 DSC diagrams of the compounds I to VII.

Compound II

FIGURE 1 (*continued*)

sition is preceded by a crystallographic phase transition.[5,12] Judging from the enthalpy and entropy values determined in the chain melting process it becomes evident that a significant degree of the organization in the lattice is lost during this process. However enthalpy and entropy values involved in this process show significant compound to compound differences although all quaternaries bear the same two long aliphatic chains which melt in the main transition. This indicates that introduction of the functional groups on the polar head of the surfactants not only affect the clearing point but they also modify the van der Waals forces involved in the conformational melting of the chains.

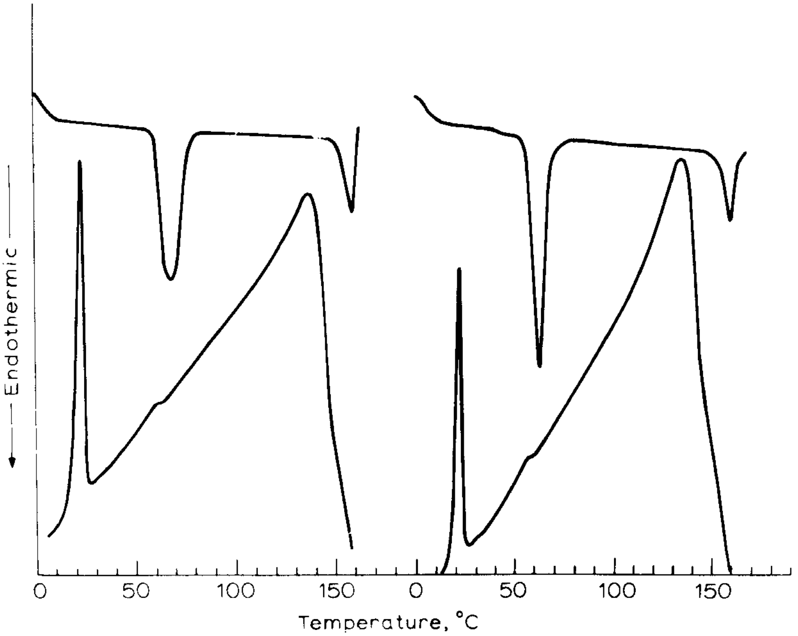
The clearing point temperatures of the functionalized derivatives are more or less constant during successive heating-cooling runs confirming the thermal stability of the surfactants. From Table I it is also



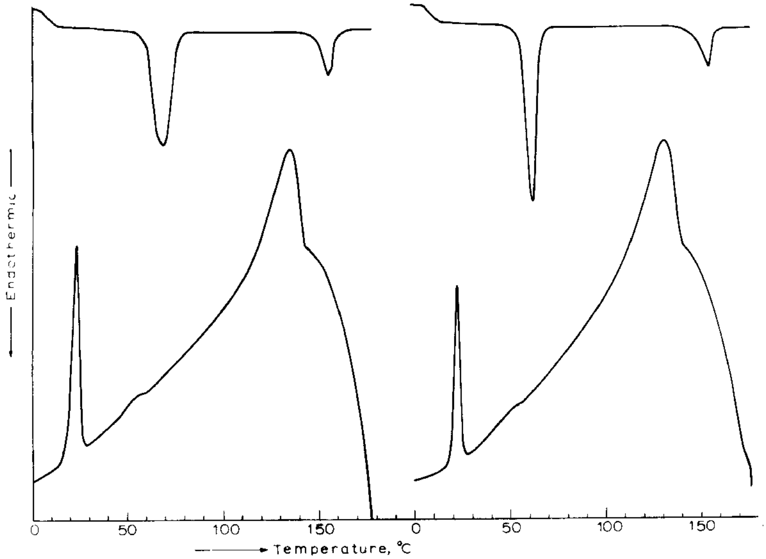
Compound III

FIGURE 1 (*continued*)

seen that the clearing point transition of the parent compound I is higher than the functionalized quaternaries. The higher clearing point temperature is due to the presence of the relatively small methyl groups, at the polar head, which apparently do not disturb the ionic bonding between quaternary nitrogens and bromides. It seems however that the introduction of the bulky carboxylic groups does not affect significantly the thermodynamic stability of the mesophase as evidenced by the high clearing point of the compounds IV and V. The same compounds also retain a high degree of order above the first transition as shown by the relatively high enthalpy and entropy changes involved at the clearing point transitions. It seems that the polar carboxylic group, located in a polar environment, does not affect unfavorably lattice interaction and therefore the enthalpy at

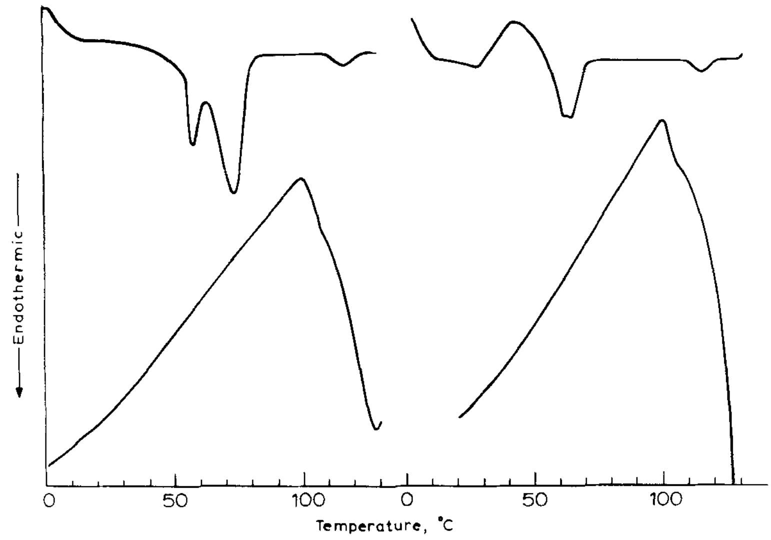


Compound IV



Compound V

FIGURE 1 (*continued*)



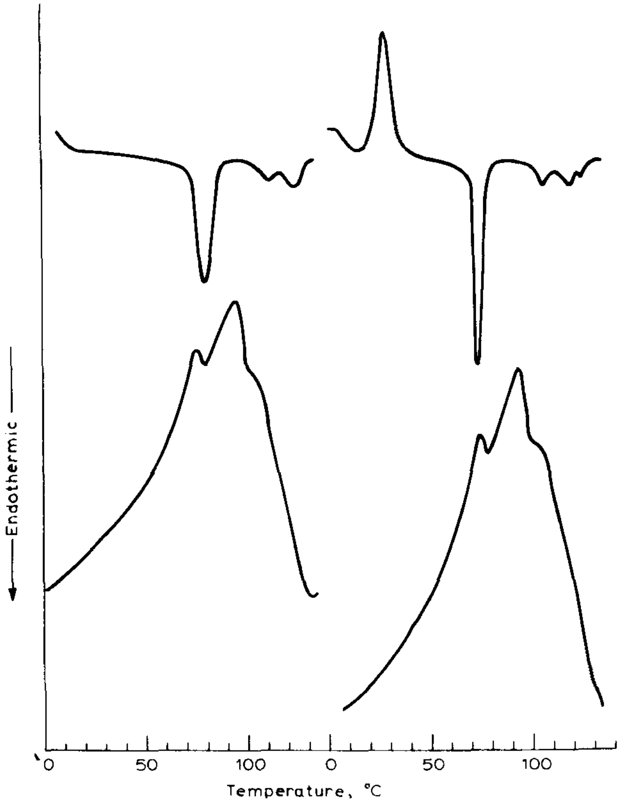
Compound VI

FIGURE 1 (*continued*)

TABLE I

Transition temperatures, enthalpies and entropies of functionalized long-chain di-*n*-alkyl quaternary ammonium salts

Compound			T,K	ΔH kJ/mol	ΔS J/K mol
I	$—CH_3$	$—CH_3$	334	40.1	120.0
			350	10.1	28.8
			439	5.1	11.6
II	$—CH_3$	$—CH_2—CH{=}CH_2$	318	44.2	138.8
			354	1.4	4.0
III	$—CH_2—CH{=}CH_2$	$—CH_2—CH{=}CH_2$	324	53.9	166.4
IV	$—CH_3$	$—CH_2COOH$	332	52.8	159.0
			420	11.8	28.0
V	$—CH_3$	$—CH_2CH_2COOH$	333	53.6	160.7
			421	13.9	33.0
VI	$—CH_3$	$—CH_2CH_2OH$	325	18.6	57.2
			331	39.0	117.7
			378	2.5	6.7
VII	$—CH_3$	$—CH_2CH_2CH_2CN$	345	28.4	82.1
			374	6.1	16.3
			383	8.0	20.9



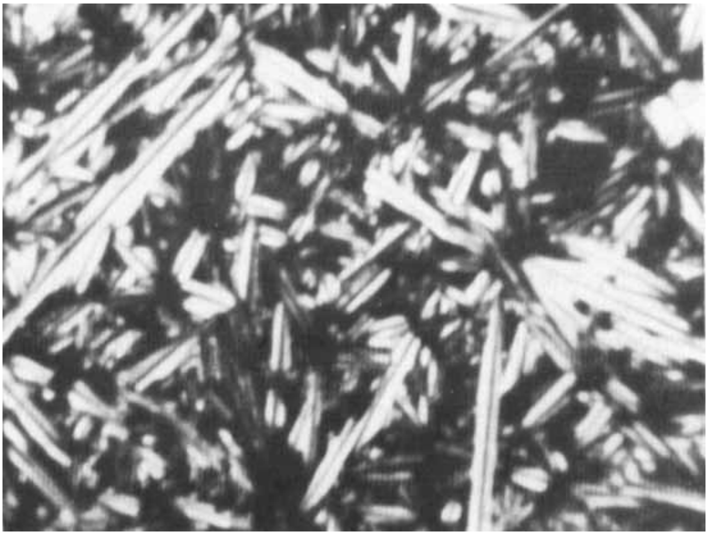
Compound VII

FIGURE 1 (*continued*)

the clearing point is relatively high. It should also be noted that the two carboxylic derivatives exhibit almost the same clearing point, a fact attributed to the predominating function of the carboxylic group in the vicinity of the ionic layers and the limited effect of the introduction of an extra methylene group in one of the derivatives.

Substitution of one or both of the methyl groups of the parent compound by less polar functional groups results in significant lowering of the clearing point (Table I). In the case of diallyl derivative the lowering of the clearing temperature is such that it almost overlaps the transition of the "melting" of the long aliphatic chains, which range between 50–70°C. On this basis the introduction of the polar —OH and —CN groups results in a differentiation between the transition of chain melting and clearing point. It is not however as effective as it is with the introduction of the carboxylic group. These results are in qualitative agreement[12] with those in which the same functional groups are attached on the quaternary nitrogen of surfactants bearing one long-aliphatic chain.

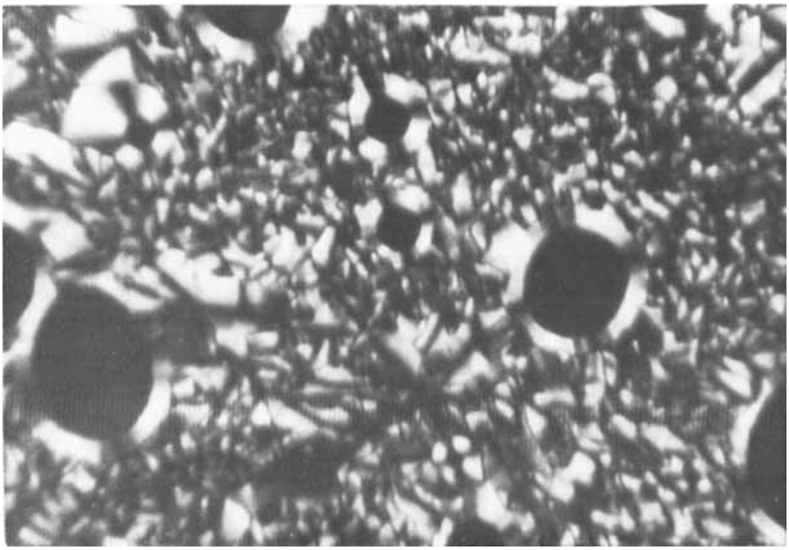
The liquid crystalline character of all the functionalized quaternaries except of the diallyl derivative (compound III) was also established by optical microscopy. Some typical liquid crystalline textures obtained on cooling are shown in Figure 2. It is interesting to notice that the mesomorphic textures were not normally observed optically after the first transition, as determined by DSC, corresponding to the melting of the chains, due to the ionic forces exercised at the polar layers which preserved the lamellar structure as in the solid phase.[13] However slight pressing of the cover-slip resulted in the appearance of the smectic phases in which the conformational freedom of the long aliphatic chains is enhanced. It seems therefore that it is appropriate to characterize these phases as smectic-like since they retain the ionic bonding of the solid phases.[13] Similar deformation behavior has also been observed for the quaternaries bearing one aliphatic chain.[11,12]



Compound I

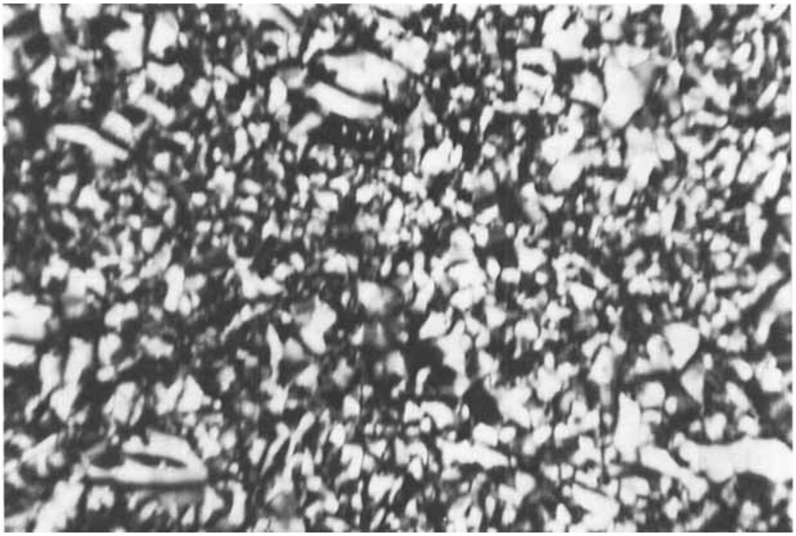
FIGURE 2 Photomicrographs of compounds I, II, IV, V, VI and VII.

Compound II

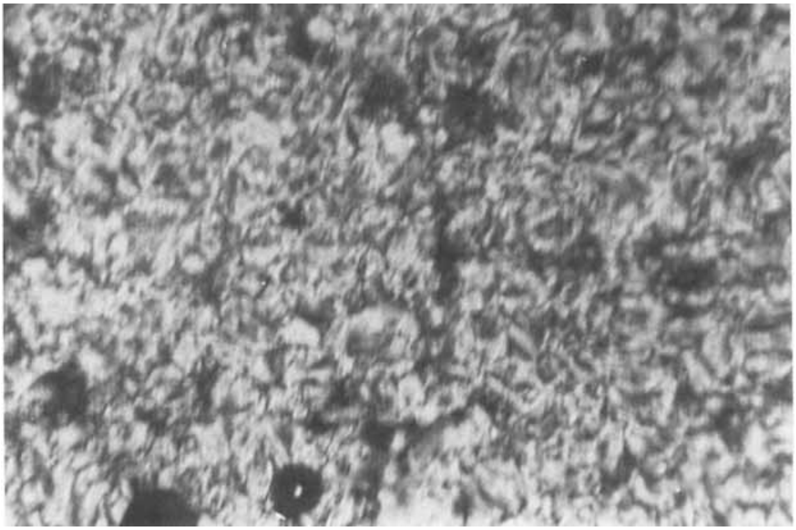


Compound IV

FIGURE 2 (*continued*)

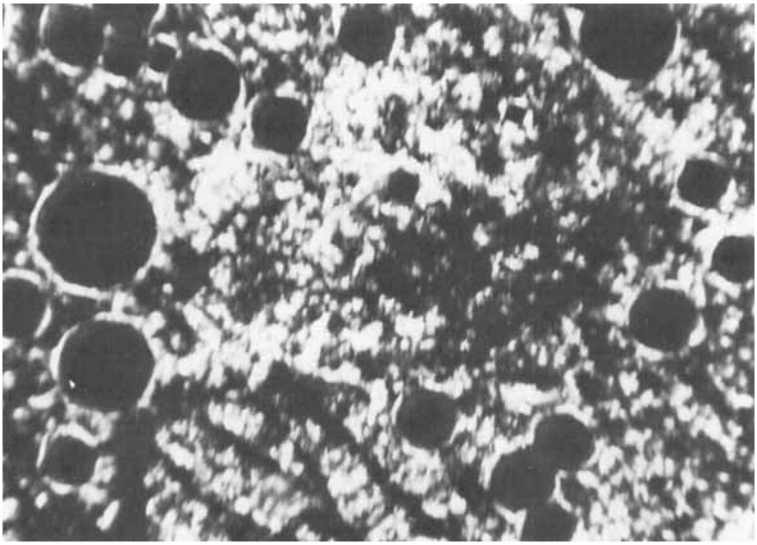


Compound V



Compound VI

FIGURE 2 (*continued*)

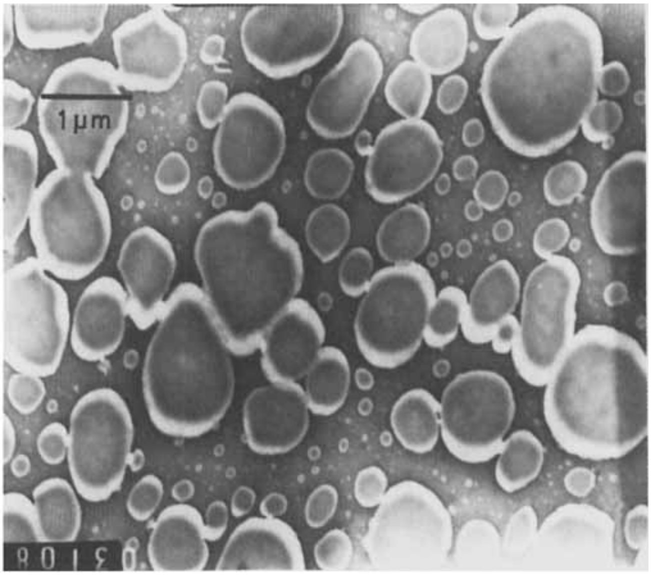


Compound VII

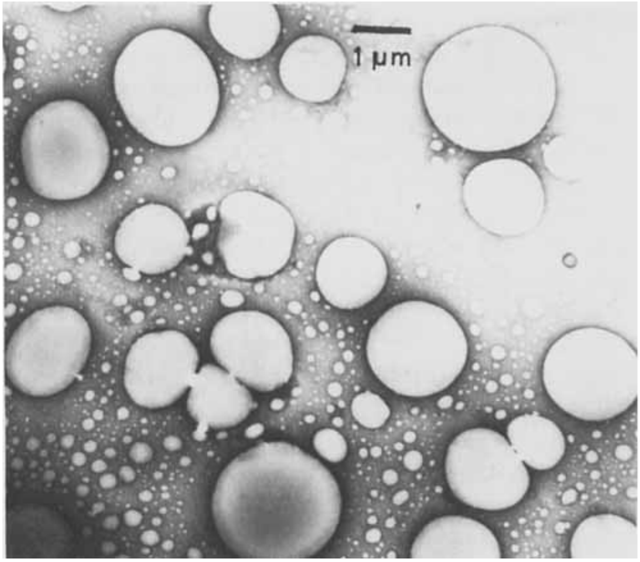
FIGURE 2 (*continued*)

The introduction of various functional groups in the polar head of the quaternary salts was also attempted in order to prepare stabilized vesicles in a more convenient way than through polymerization of monomeric vesicles. The latter mode does not always lead to stable vesicles, due to unfavorable accommodation of the main-chain with the pendant groups. Concerning the quaternaries of this study it has been found that in addition to the parent compound I, that forms[16] vesicles in water, compounds II and III also form[14] vesicles. In Figure 3 are shown vesicles resulting from the dispersion of surfactants VI and VII in water. Vesicles were not however formed from compounds IV and V both in neutral and alkaline media. In the latter case, due to neutralization of the carboxylic group they become zweiterionic. Although it is difficult to rationalize, at the moment, this differentiation in behavior as compared to other surfactants of the series it is however clear that modification of the polar head has a profound effect on the ability of quaternaries to form vesicles. The behavior of carboxylic substituted surfactants is rather unexpected and further work is required before general conclusion can be drawn concerning the property of these surfactants to form vesicles.

In conclusion the structural characteristics which induce the formation of thermotropic liquid crystalline phases are also responsible



Compound VI



Compound VII

FIGURE 3 Electron micrographs of compounds VI and VII.

for the well-known smectic mesophases exhibited by vesicles. It is also clear that the functionalization of long-chain di-*n*-alkyl quaternary ammonium salts has a profound effect on their smectic behavior and their ability to form vesicles. Concerning the thermotropic phases, the thermodynamic stability is dependent on the polarity of the functional groups. However, it is not possible, at the moment, to determine the factors or rather the functional groups which affect the formation and stability of vesicles in water for these series of surfactants.

References

1. J. H. Fendler, In "*Membrane Mimetic Chemistry,*" Wiley-Interscience, New York, (1982) and references cited therein.
2. H. Kelker and R. Hatz, In "*Handbook of Liquid Crystals,*" Verlag Chemie, Weinheim, (1980) and references cited therein.
3. A. E. Skoulios and V. Luzzati, *Acta Cryst.*, **14**, 278 (1961).
4. D. Chapman and D. T. Collin, *Nature*, **206**, 189 (1965).
5. K. Iwamoto, Y. Ohnuki, K. Sawada and M. Seno, *Mol. Cryst. Liq. Cryst.*, **73**, 95 (1981).
6. D. Chapman, *Pure and Appl. Chem.*, **50**, 627 (1978).
7. V. Busico, P. Cernicchlaro, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1983).
8. G. F. Needham, R. D. Willett and H. F. Franzen, *J. Phys. Chem.*, **88**, 674 (1984).
9. J. D. Gault, H. A. Gallardo and H. J. Müller, *Mol. Cryst. Liq. Cryst.*, **130**, 163 (1985).
10. A. Malliaris, C. Christias, G. Margomenou-Leonidopoulou and C. M. Paleos, *Mol. Cryst. Liq. Cryst.*, **82**, 161 (1982).
11. C. M. Paleos, G. Margomenou-Leonidopoulou and A. Malliaris, *Chimika Chronika*, New Series, **14**, 89 (1985).
12. G. Margomenou-Leonidopoulou, A. Malliaris and C. M. Paleos, *Thermochimica Acta*, **85**, 157 (1985).
13. V. Busico, A. Ferraro and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **128**, 243 (1985) and references cited therein.
14. D. Babilis, P. Dais, L. H. Margaritis and C. M. Paleos, *J. Polym. Sci., Chem. Edit.*, **23**, 1089 (1985).
15. V. Busico, D. Castalso and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **78**, 221 (1981).
16. T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, **99**, 3860 (1977).
17. J. Geordeler in "*Methoden der Organischen Chemie*" (Houben Weyl), Vol X1/2, Georg Thieme, Verlag, Stuttgart, 1958 p. 591.